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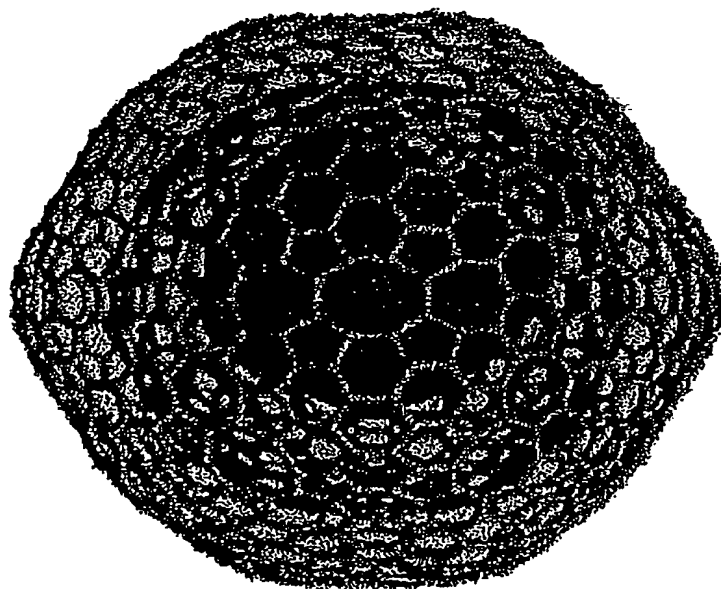
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[Continued on next page]

(54) Title: MICROPARTICLES AND METHODS OF MAKING THEM



(57) Abstract: Microparticles having a ferromagnetic core encapsulated in a graphitic curved shell containing hetero atoms are prepared by providing a solution containing source material of a ferromagnetic metal, carbon and the hetero atoms e.g. N, forming solidified particles containing source material of the ferromagnetic metal, carbon and the hetero atoms from the solution, and pyrolysing the solidified particles in inert gas so as to form the ferromagnetic core and said encapsulating graphitic coating. Small particles, e.g. of core size 10 - 150 nm, having good particle size distribution can be obtained, which are useful in catalysis.

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MICROPARTICLES AND METHODS OF MAKING THEMFIELD OF THE INVENTION

5 The present invention relates to microparticles and in particular to those in the nanoparticle range, and to use of such particles in catalysis, as well as methods of making them.

BACKGROUND OF THE INVENTION

10 It has been known to be desirable for some time that solid microparticles having catalytic activity should be preferred for liquid phase catalysis, because on the one hand macro catalysts have clear disadvantages from the point of view of atom efficiency, while soluble
15 catalysts, although theoretically efficient, present great difficulties of separation.

However, the desire for the microparticles to be as small as possible so as to achieve the greatest possible efficiency conflicts in principle with the ease of
20 separating them from the liquid reaction medium, if for example filtration or like methods of separation are attempted.

It is for this reason that there has been interest in magnetically susceptible catalytic microparticles
25 which are dispersible in the liquid reaction medium but which are able to be coagulated under the influence of a magnetic field and thereby readily separated from the medium. They can then be re-dispersed for re-use.

However, the problem then arises that many
30 ferromagnetic materials would react with the reaction mixture; it is therefore necessary to protect the ferromagnetic particles by a coating of some material which is inert to the medium.

In JP-A-02069904, for example, there is disclosed a way of "rust-proofing" a magnetic metal powder by contacting the preformed powder with carbon monoxide, methane or ethane and hydrogen at high temperatures. It is stated that the saturation magnetizations of the magnetic metal films (sic) obtained is not lowered substantially.

Another method which has been used is that of an arc discharge. In IEEE Transactions on Magnetism, 32, No. 5 of September 1996 at page 4511-4513, Jeyadevan et al, after reviewing earlier attempts at encapsulation using arc discharges proposed to coat pre-existing magnetic particles with a surfactant and then treat them in an arc so that the surfactant is reduced or decomposed to a carbon that encapsulates the magnetic particles. The size of the magnetic particles was stated to be an average diameter of 10 nm and the surfactant used was sodium oleate.

Turgut et al J. Appl. Phys. 81 (8) of April 1997 at pages 4039-4041 disclose another arc discharge process and state that in this case many of the particles were only nominally coated or uncoated. The interest in that disclosure concerned the crystalline structure of the magnetic nanocrystals. All of these processes have extremely low yields but also use extremely high temperatures (arc temperatures).

The present inventors believe that these prior art processes produce many different forms of carbon or, if a graphite layer is produced, it has defects and/or has curvature due to the presence of five-membered carbon rings which distort the graphite structure.

Yet another approach is seen in WO-A-99/46782 of Universiteit Utrecht. The inventor is Geus, and this

document will be preferred to as "Geus" hereafter. This takes an approach different from that of the rest of the prior art. Ferromagnetic material is deposited on the surface of an alumina support. A graphite coating is then applied and the alumina support is dissolved away leaving particles which are allegedly entirely coated with graphite. The Geus disclosure will be discussed in more detail later.

However, it is clear from the above that all prior processes have been ones which require complex preparative stages before the coated ferromagnetic microparticles were achieved.

SUMMARY OF THE INVENTION

In contrast, we propose a direct method for the formation of ferromagnetically nucleated graphite-protected microparticles. Furthermore, we find that this method can provide particles within a close size range and with little or no loss in magnetic susceptibility as compared to the pure magnetic material.

After the microparticles have been prepared, catalytically active components such as a noble metal, e.g. palladium metallic clusters, can be supported on the external surface. This results in a highly active carbon-supported catalyst for chemical reactions, for example hydrogenation reactions, in the liquid phase.

The chemically and mechanically robust microparticles (usually in the nanoparticle size range) are shown to disperse well in aqueous or organic solvent and form a stable dispersion and exhibit an excellent and consistent mass transfer so as to sustain a high catalytic rate of reaction.

We find that the coating has very high coherence so that the core is not exposed to the reagent, there is high yield and, as already mentioned, there is a high degree of uniformity of size.

5 The invention in one aspect therefore provides a method of forming microparticles with a ferromagnetic core encapsulated in a graphitic shell containing hetero atoms, which includes the steps of providing a solution containing source material of a ferromagnetic metal,
10 carbon and hetero atoms, forming solidified particles containing source material of the ferromagnetic metal, carbon and the hetero atoms from said solution, and pyrolysing said solidified particles in inert gas so as to form said ferromagnetic core and said encapsulating
15 graphitic coating containing hetero atoms.

In a second aspect the invention provides microparticles having a ferromagnetic core encapsulated by a graphitic curved shell containing hetero atoms.

The process typically involves the solidification of
20 a solution, e.g. droplets of the solution, containing soluble salt(s) or complex(es) of the ferromagnetic element(s) or alloy(s) and decomposable sources of carbon and of a hetero atom such as nitrogen, and pyrolysis of the solids to form a graphitic/hetero encapsulating shell
25 around a ferromagnetic core. The source of carbon and of the hetero atom is preferably the salt or complex itself/themselves. For example cyanides, isocyanides, cyanates or isocyanates, especially as ligands, are decomposable in the pyrolysis to yield a graphitic shell
30 including nitrogen atoms.

It is believed that the presence of the metal or metals, particularly Fe, Co, Ni or Pd, catalyses the formation of the graphitic shell (which is usually multi-

layer). Suitable metals for the core are for example, Fe, Ni, Ca, Zn, Cu, Mn, Mg, Co, Pd, Pt, Ti, Mo and V and at least one metal selected must be ferromagnetic. Use of two or more metals is preferred. One metal may be present in the solution in or as a cationic species, the other in an anionic species, such as a complex anion. Suitable counterions for these species are typically also present.

The pyrolysis is performed in inert gas, such as N₂ or Ar. An inert gas is one which does not chemically react with the particles at the pyrolysis conditions. The pyrolysis temperature must be sufficient to form the core and the graphite coating or shell, preferably so that the shell has a graphitic structure only. The phase or phases formed in the core in the pyrolysis depend on the pyrolysis treatment and also on the metal or metals present. In some cases elemental metal or alloy phase cores are formed, e.g. Fe, Fe-Ni, Fe-Co, Co-Pt, Co-Ni whereas in other cases mixed phases are formed which may be elemental metals (e.g. Fe and Cu phases) or carbide. A carbide only core, such as Fe₃C, or a mixture of carbides, e.g. carbides of Fe and Mn, Fe and Zn, Fe and Ca, may be formed.

N is preferred as the hetero atom. Other hetero atoms which may be used are, for example, B, P, S, or O.

The formation of the solidified particles may be achieved by first dividing the solution into droplets, e.g. by forming a spray. Solidification of the droplets may be the first phase of pyrolysis; or it may be a precipitation occurring as a result of contact with a precipitant such as, for example, ammonia or other alkaline solution. Alternatively chemical precipitation of particles from the solution may be performed in bulk,

e.g. by changing the pH of the solution by addition of alkali, and separation of the particles. Use of droplets improves the size distribution of the particles, i.e. allows controlled size and narrow size distribution.

5 Typically the formation, e.g. precipitation, of the particles from the solution in the process of the invention is performed in the absence of other solid particles, i.e. heterogeneous particles not dissolved in the solution (such as nucleating or seeding particles).

10 The solution may further contain a diluent source or precursor forming on pyrolysis a diluent for the microparticles, e.g. an amorphous matrix. Decomposable diluent sources include polyvinyl alcohol (PVA), preferably partially hydrolysed, polyvinyl pyrrolidone
15 (PVP) or other polymers. Inorganic sources, especially of calcium, may also form diluent material outside the microparticles. The sources may act to dilute the ferromagnetic and graphitic source species to prevent wasteful agglomeration of microparticles via their
20 graphitic layers. The amorphous mass may contain individual microparticles distributed through it.

 To prepare catalytically-active particles, the carbon surface, either of the microparticles or of a diluent matrix containing them, may be functionalized
25 e.g. by acid treatment, for carrying catalytic functions such as metals. These catalytic functions may be added by conventional procedures.

 Particular solution systems may be as follows:

 Nickel-iron alloy microparticles can be prepared
30 from iron nitroferricyanide $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ -nickel nitrate solution. Other systems include Fe/Ca; Fe/Zn, Fe/Cu, Fe/Mn, Fe/Co, Fe/Ni, Fe/Mg, Fe/Pt composites, or

their carbides, oxycarbides, oxides and mixed oxides as inner cores within the encapsulation.

Typically, other carbon-coated Fe based alloys or mixed composites cores can be prepared via an aqueous solution of iron cyanide containing precursor,
5 $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ mixed with aqueous solutions of $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{PtCl}_4(\text{NH}_4)_2$ (in a 1:1 Fe:M molar ratio), respectively.

10 In many of these systems there is variability in the metal/carbon atomic content of the salt or complex. Adjustment of this ratio affords a means of adjusting the average thickness (number of layers) of encapsulation graphite.

15 An additional step of treatment of the particles with acid after pyrolysis is beneficial. Firstly it removes metal impurity, i.e. metal which has not been fully encapsulated in graphite and which may affect catalytic properties. Secondly, the acid treatment can
20 add functionality to the graphite surface. Alkali treatment, with or without oxidising agent, e.g. bleach, may be employed to add functional groups.

The microparticles are characterized by the presence of hetero atoms (usually nitrogen, but possibly B, P, O, etc.) in a graphitic carbon shell surrounding and
25 encapsulating the ferromagnetic core. Preferably the hetero atom content in the graphitic shell is at least 1 atom %, a suitable maximum being 10 atom %. Typically the content is 2-7 atom %. Otherwise, apart from trace
30 impurities, the shell is carbon. These hetero atoms provide curvature, analogous to that of fullerene, so that a more complete enclosure of the core is achieved without the faults or fractures of a purely graphitic

structure. It is believed that the incorporation of the chemically bound hetero atoms into the graphite molecular structure causes this curvature of the graphite layers. Since the graphite layer is normally planar, deviation
5 from planar forms in pure graphite is obtained by defects such as fracture or discontinuities, or possibly by the presence of five-membered carbon rings as mentioned above. By incorporating hetero atoms in sufficient amount to cause curvature, in this invention, a stable
10 high-quality coating or shell with minimal defects is obtained.

The number of carbon layers in the graphite coating may be 1 to 1000, more preferably 1 to 100. A plurality of layers is usually formed. The thickness of each layer
15 is about 0.34 nm.

The cores of the microparticles preferably have an average diameter in the range of 5 to 500 nm, more preferably 10 to 150 nm, most preferably 10 to 50 nm.

The more complete covering afforded by the carbon
20 shell and the regularity of size of the particles are great advantages in the context of liquid-phase catalysed reaction.

With such small magnetic catalyst bodies, the advantages of homogeneous (or colloidal) and
25 heterogeneous catalysis may be combined since, while there is no agglomeration, the catalytic sites per area on the small particle are optimised and very well accessible. Application of external magnetic field leading to agglomeration of these magnetic particles
30 facilitates their separation from product. Apart from catalysis application, other useful applications of such carbon-encapsulated nanometer sized particles may also be expected in several fields of technology.

The invention further consists in use of the microparticles described above in catalysis, for example hydrogenation. For this purpose, the microparticles typically carry catalytically active metal on their surface i.e. on the carbon shell and/or on the amorphous diluent incorporating the microparticles.

BRIEF INTRODUCTION OF THE DRAWINGS

In the accompanying drawings:

Figure 1 is a schematic diagram of a nano-size soft magnetic alloy encapsulated in quasi-spherical graphitic shells;

Figures 2a and 2b (comparative) are X-ray diffraction patterns for Geus particles before and after acid treatment, respectively;

Figures 3 and 4 (comparative) are respectively high (x 800,000) and low (x 46,000) transmission electron microscope (TEM) micrographs of Geus particles;

Figure 5 is an X-ray diffraction pattern (XRD) of the particles of Example 2 of the invention after acid treatments;

Figure 6 is a low-resolution TEM micrograph of a present sample before pyrolysis;

Figure 7 is a high resolution TEM micrograph of present particles after pyrolysis;

Figure 8a is an X-ray photo-electron spectroscopic (XPS) record demonstrating the presence of hetero atoms in the shell;

Figure 8b is an XPS spectrum of the N region of the particles before heating;

Figure 9 is a vibrating sample magnetometer (VSM) graph of a present sample before acid functionalization;

Figure 10 is a graph showing the catalytic activity of a present catalytic sample;

Figure 11 is an XRD spectrum of a second embodiment of particle after pyrolysis;

5 Figures 12 and 13 are a low resolute TEM micrograph of the second embodiment before and after pyrolysis respectively;

Figure 14 is a high resolution TEM micrograph of the second embodiment after pyrolysis;

10 Figures 15 and 16 are VSM and EDX records respectively of the second embodiment after pyrolysis;

Figures 17 and 18 are high- and low-resolution TEM micrographs respectively of particles of a third embodiment;

15 Figure 19 shows magnetic responses (VSM) of particles obtained in examples of the invention; and

Figure 20 shows rates of a hydrogenation reaction catalysed by particles.

20 EXAMPLES

System Example 1 (comparative)

Preparation of carbon encapsulated nickel-iron nanoparticles on a solid support (alumina) via gaseous methane decomposition (Geus method)

25 We adopted and modified the method of Geus. Alumina-supported nickel-iron alloy particles were prepared by a general controlled deposition-precipitation method as follows: a solution containing nickel compound was prepared by dissolving 2.0 g of nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into 10.0 ml of deionised (DI)
30 water. 4g of activated alumina were added to the solution and the pH was adjusted to 5. An aqueous solution containing iron compound (2g of sodium

nitroferricyanide (III) dihydrate $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}]$ in 10.0 ml DI water was then added to the mixture at a rate of 1 ml/min under vigorous stirring giving in total 1:1 molar ratio of Ni:Fe. The solid material was filtered, extensively washed, dried overnight at 120°C and calcined at 300°C in a flowing stream of 30 ml/min air for 3h. Formation of alloy particles on alumina was conducted by controlled reduction of the solid at 700°C (with a temperature programmed ramping from room temperature to 700°C at 6°C/min) under a flow rate of 100 ml/min 20% H_2 in nitrogen for 2h. Deposition of carbon was then carried out by placing the solid at 700°C in a stream of 20% methane in nitrogen at a total flow rate of 100 ml/min. After completing the carbon encapsulation the resulting solid was cooled to room temperature in a flow of nitrogen. The alumina support was allowed to dissolve in boiling concentrated HCl at 120°C for 15h. The solid was collected, exhaustively washed and dried.

Synthesis Example 2

Preparation of carbon encapsulated nickel-iron nanoparticles directly from solution (inventive method)

Three aqueous solutions (2g of nickel (II) nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 10.0 ml of DI water; 1 g of polyvinyl alcohol of MW 31,000 to 50,000 in 100 ml DI water; 2g of sodium nitroferricyanide (III) dihydrate $[\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}]$ in 10.0 ml DI water) were mixed together. The solution mixture was allowed to pass to the pneumatic sprayer head kept at 20 psi (140 kPa) N_2 gas. A fine mist of this solution mixture was sprayed into the headspace of a jar filled with 0.88 sg (specific gravity) saturated ammonia solution. The fine droplets immediately form solid precipitates when in contact with

ammonia (vapour and solution). The solid was then collected, centrifuged, extensively washed in ethanol, dried in air at room temperature and calcined at 900°C for 10h with temperature increase at 10°C/min. During calcination N₂ is passed at 100 ml/min. Before the characterization described below, the microparticles produced by the calcination are purified by immersion in dilute HCl for 3h at room temperature.

10 **Synthesis Example 3**

Preparation of carbon encapsulated nickel-iron nanoparticles directly from solution (inventive method)

The fine mist particles generated as in Synthesis Example 2 but from a solution lacking PVA were sprayed directly into a hot zone of a furnace at 900°C with a counter current of N₂ at 15 ml/min. As they enter the zone the droplets solidify and then fuse and calcine as before to yield nanoparticles encapsulated by graphitic/hetero atom layers as before.

20

Synthesis Example 4

Fe/Ca system leads to carbon-encapsulated Fe₃C nanoparticles (inventive method)

The same iron source, Na₂Fe(CN)₅NO.2H₂O, is used as in the previous examples. An aqueous solution of this iron precursor is mixed with an aqueous solution of Ca(NO₃)₂.4H₂O in a 1:1 Fe:Ca molar ratio and treated by the spray precipitation protocol of Example 2. Polyvinyl alcohol is not included.

30 The Fe/Ca system enables the obtaining of a very high concentration of carbon-encapsulated nanoparticles with a very narrow size distribution. The XRD spectrum (Figure 11) shows that this sample consists of Fe₃C

nanoparticles encapsulated in concentric graphitic carbon layers with $\text{Ca}(\text{OH})_2$, CaCO_3 and related Ca-containing species. Energy Dispersive X-ray analysis (EDX)

indicates the presence of Ca and iron rich material

(Figure 16). The Cu peak is from the container holding the sample. TEM micrographs of the sample after

calcination show that the iron carbide nanoparticles are encapsulated in graphitic carbon (Figures 12-14), the amorphous calcium-containing phases forming matrices

between the graphitic-coated iron carbide particles (Figure 13). We attribute this to the fact that calcium would not form a stable alloy with iron (compare Fe-Ni) but its presence with the Fe-based nanoparticles (Figure 14) protects the composite material from sintering during the heat treatment in N_2 , hence providing a very high concentration of carbon coated iron containing nanoparticles with a very homogeneous size.

Microanalysis of the product shows that it contains Ca- 35.49wt% and Fe- 29.57wt%. Adding excess acidified water to the final material allows removal of particularly the calcium-containing matrix (63.3mg Ca and 37.06 mg Fe could be leached out from 200 mg solid in the 50mL HCl solution), releasing the tiny colloidal graphitic carbon-encapsulated magnetic Fe_3C nanoparticles. These carbon coated particles contain Ca 3.6wt% and 10.89wt% Fe.

Iron carbides Fe_2C , $\text{Fe}_{2.2}\text{C}$, Fe_5C_2 and Fe_3C all are ferromagnetic, displaying a high coercive force. Fe_3C is known to give a high magnetic response but its extreme air sensitivity limits its uses. It is of high interest that this technique can prepare macroscopic quantity of magnetic carbon-encapsulated iron carbide nanoparticles. Figure 15 shows that our sample displays a saturation magnetization of 90 emu/g. It is apparent that this

material is quite air-stable; presumably the graphite coating offers protection against oxidation.

TEM imaging (Figures 17,18) clearly shows graphitic encapsulation of other systems such as Fe/Mn indicating the generic nature of the method.

Synthesis Example 5

Noble metal deposition onto the carbon nano-materials

The catalyst component (heterogeneous catalyst or homogeneous catalyst species) may be directly deposited onto the external surface of the carbon coated nano-magnet composites. However, it is desirable to functionalise the external carbon surface. Accordingly, the surface of the carbon encapsulated alloy particles prepared by the method of Example 1 on the one hand or Examples 2 or 3 on the other was functionalised with -OH or -COOH groups by immersing them into boiling concentrated HCl (acid treatment) or diluted bleach (NaOCl with and without H₂O₂) solution. For some applications an acid or bleach washing step is advantageous to remove traces of uncoated metal or metal oxide. The surface activated carbon particles were then collected, washed and dried. A wetness impregnation method was then applied in order to deposit 5% Pd onto these carbon based materials (an appropriate amount of Pd (II) acetylacetonate was allowed to dissolve in acetone/water mixture at pH 10 and then stirred with the solid for 3 h at room temperature; the solid was then collected after extensive washing with acetone and air drying at room temperature).

Example 6: Catalyst testing

6.5 ml of nitrobenzene was dissolved into 125.0 ml of isopropanol (IPA) as a solvent (well dispersed) and was placed in a glass beaker inside a 300 ml batch stainless steel Parr reactor. 30 mg of the carbon-based catalyst was then added. The reactor was purged with a nitrogen flow for 5 minutes followed by intermittent purges with pure H₂ at 2000 kPa (20 bar). This ensured that the reactor was actually filled with pure H₂ without trapping any other gases. The reactor was kept at 2000 kPa (20 bar) and heated up to 80°C with constant stirring. Samples (<1 ml) were collected at different times from the reactor via the internal sampling dip tube without seriously disturbing the on-going reactions. The samples were analyzed by HPLC. For the hydrogenation of nitrobenzene, aniline was the major product observed.

Example 7: Material characterization

In order to determine the formation of Fe-Ni alloy and graphitic carbon structure X-ray powder diffraction (XRD) was carried out. XRD patterns were recorded at room temperature using the Cu K α radiation ($\lambda = 1.54056 \times 10^{-10}$ m).

The materials were also examined using a Philip CM20 high-resolution transmission electron microscope (TEM) operating at accelerating voltage of 200kV. Samples were suspended in isopropanol. A few drops of the suspended solution were put onto a copper grid covered with a holed lacey carbon film prior to examination.

Magnetic measurements were performed using a vibrating sample magnetometer (VSM), which consisted of an electromagnet (maximum applied field of $\pm 1200 \text{ kAm}^{-1}$) with a sample cell holder vibrating between two pole

faces. Powder samples were prepared by placing a small amount of wax in the base of a brass sample holder, followed by topping it with approximately 50 mg of the powder sample. The powder was set in place by dripping a small amount of molten wax on top and then plugging with a brass stopper, which was then put into a Perspex outer sheath. The sample was then aligned by placing the holder in boiling water to melt the wax and cooled in an applied field of 2T. The sample was then magnetised to saturation in a pulsed magnetic field (up to 9T) parallel to the direction of measurement. The sample was held at the end of a rod linked to an oscillator, causing the sample to vibrate in a direction perpendicular to the applied field between detection coils positioned on the pole tips of an electromagnet. A current was passed through the coils of the electromagnet producing an applied field that was measured using a Hall probe. Various fields were applied allowing time for the field to stabilise each time, thus eliminating any signals being produced in the coils due to the applied field. the vibration of the sample generated an AC signal from the coils proportional to the magnetisation of the sample. A frequency of 70-80Hz was used, as there was a minimum of background noise in this range. Hence, the VSM measured the difference in magnetic induction between a region of free space with and without the sample as it vibrated giving a direct measure of the magnetisation M . While the sample is in the magnetic field the magnetic induction was $B_M = \mu_0(H+M)$ as the sample was moved away. This changes to $B_0 = \mu_0 H$, which gave the change in magnetic induction $\Delta B = \mu_0 M$, B - magnetic induction, H - magnetic field, M - magnetisation, μ_0 - permeability of free space.

Temperature programmed oxidation was carried out using a purpose-built apparatus. Carbon sample (50 mg) was sandwiched between two silica wool plugs in a quartz reactor tube housed in a temperature controlled tubular furnace. Diluted air (5% O₂) was allowed to flow through the sample at a constant flow rate (2 ml/min). A quadruple mass spectrometer was used to monitor the exit gas (mass fragments) continuously without much delay since the dead volume between the mass spectrometer and the reactor tube was carefully minimised. The sample was ramped at 10°C/min from 150 to 400°C and then 2°C/min from 400 to 900°C under the same flow rate. Since different forms of carbons (amorphous, tubular, graphitic, enclosed) react with oxygen at different temperatures (different in chemical reactivity), hence with calibration their differentiation is achieved.

Results of Material Characterization

A: Geus method - Synthesis Example 1

XRD measurement (Figure 2a) on the calcined alumina-supported cyanide precursors after H₂ reduction and methane treatment as according to Geus show clearly the characteristic peaks of graphitic structure ($2\theta = 26.63^\circ$, $d = 3.345$), FeNi (1:1) alloy ($2\theta = 43.73^\circ$ and 50.93° with $d = 2.069$ and 1.792 , respectively) and alumina ($2\theta = 67.33^\circ$). No peak is matched to individual metal (for Fe, $d = 2.027$ and 1.433 ; for Ni, $d = 2.034$ and 1.762) or metal oxide peaks (for Fe₂O₃, $d = 2.518$ and 2.953 ; for NiO, $d = 2.088$, 2.412 , 1.477 and 1.476 ; for (Ni, Fe) Fe₂O₄, $d = 2.520$, 1.479 , 1.610 , 2.950 and 2.091) suggesting alloy (FeNi with $d = 2.080$ and 1.800) is favourably formed on the porous alumina support. The calculated average particle size of the alloy after

accounting for the instrumental peak broadening is about 36.6 nm.

Acid treatment of this material leads to retention of 6.1% wt of acid insoluble material (Geus/methane/ 850°C). The XRD measurement (Figure 1b) clearly indicates that the alumina support is removed (peak at $2\theta = 67.33^\circ$ removed) by the acid treatment; however, it also appears to dramatically reduce the alloy intensity relevant to graphitic structure and shifts the average alloy particle size to 16.7 nm.

TEM clearly shows that some alloy particles are encapsulated in polygonal graphitic structures (Figures 3 and 4); however, their size distribution is extremely broad (10 to 200 nm). Energy Dispersive X-Ray (EDX) analysis confirmed the presence of Fe and Ni. The number of the encapsulated graphitic layers vary from particle to particle and more than 15 layers of carbons are commonly found. Also, there are many other forms of carbon structures (amorphous, graphitic, tubular, whisker, fibres, onions, encapsulated carbons, etc.) observed. After the acid treatment the alumina support and incomplete carbon coated metal/metal oxide are removed. The final product contains mainly carbon structures (tube, amorphous, fibres, onions, etc.) the principal form of which is found to be the tubular carbon. It is noted that there is very small amounts of carbons still containing metallic inner cores present in the final product.

B: Product of method embodying the invention - Synthesis Example 2

XRD measurement (Fig. 5) clearly indicates the presence of alloy peaks ($2\theta = 43^\circ$ and 51° with $d = 2.07$

and 1.79, respectively) in a correct intensity ratio. The calculated average particle size is considerably smaller than the material prepared by the Geus method. In order to provide a carbon support to each of these coated alloy nanoparticles soluble polyvinyl alcohol (PVA hydrolysed, MW 31,000 to 50,000) is added to the solution prior to spraying. Polyvinyl alcohol is known to decompose readily at elevated temperatures (ca 120°C). Hence it is a carbon source for an amorphous matrix. XRD in Figure 5 shows that the calculated average encapsulated core size is 11.0 nm with the three distinctive Fe:Ni alloy peaks. There is only a very small broad hump near the 2θ of 26° indicating consistently only a few atomic layers (even after pyrolysis of the composite material at 900°C). 35% wt of insoluble material is retained under identical acid treatment conditions as were employed for the Geus samples.

Figure 6 shows a typical low-resolution TEM micrograph of the present precipitation sample. It is interesting to see many nanoscopic size particles with a very uniform particle size distribution. The particle contains Fe and Ni as confirmed by EDX analysis. Direct measurement on the micrograph shows that a majority of the encapsulated particle cores are in the size range of 10-15 nm. Figure 8b shows the N region in an XPS spectrum.

High resolution TEM micrographs (Figure 7) indicate that all the particles after pyrolysis are found exclusively encapsulated in the quasi-spherical graphitic structures. These graphitic encapsulated particles are embedded in amorphous carbon material (the relative amount depends on the amount of polyvinyl alcohol used).

Detailed examination of the quasi-spherical carbon coatings show that in many cases, carbon lattice fringes (ca. 3.4×10^{-10} m) could be traced, yielding surprisingly concentric carbon shelled structures. Only short exposure of the selected area to the electron beam is ensured (<60 s) to ensure that there is no possibility of carbon shelled structure formation being due to the electron beam illumination. Attempts to obtain a lattice image of the core particle were not successful on a Philips CM20 TEM microscope. It is believed that the fringe separations of the alloy particle (2.09×10^{-10} m, 1.79×10^{-10} m) are beyond the resolution of the microscope used ($>2.4 \times 10^{-10}$ m).

Figure 8a shows XPS survey spectra of carbon-coated FeNi nanoparticles after encapsulation at 900°C but before acid treatment to remove any non-fully encapsulated particles. An XPS survey was recorded on the sample without pre-treatment (before heating) and after it has been heated *in situ* at 250°C for 30 minutes to desorb some possible contaminants. No major changes are observed in the resulting data. The spectra are very similar - upper line being before treatment and lower line after - showing the reproducibility of this measurement. All binding energies are given with an uncertainty of 0.2 eV on the absolute value. No charge effect being observed, the peaks are directly referenced to the carbon C1s peak at 284.6 eV.

It appears that the surface (or the first few atomic layers) contains essentially carbon but also with a small amount of other hetero-atoms (O, N, Na, Fe, Ni, etc). We detected small signals of Fe and Ni 2p and Auger peaks with the C:Fe and C:Ni atomic ratios being at around 0.05. This fact agrees with the TEM images in showing

that the Fe/Ni are species totally encapsulated by carbon cages after heat treatment in N₂ at 900°C because their signals are not strong. The binding energies of these exposed Fe and Ni species suggest that they are unlikely to be in metallic states. An oxygen signal is also found. It is not yet clear whether O is attached to the exposed iron/nickel species, or to nitrogen or carbon. Also, there are traces of sodium (Nals peak) in the calcined sample which probably came from the iron precursor used.

It is interesting to find that a nitrogen signal is observed. The surface contains nitrogen in an atomic ratio of 43:3 C to N. The N1s region (Figure 8b) consists in a main peak at 398.6 eV with a shoulder at 400.8 eV. It has been reported that a N1s signal at 401 eV is characteristic of nitrogen atoms present in graphene sheets. It is thus concluded that a small amount of nitrogen is incorporated into the graphene network. It has also been reported that a strong peak at 398 eV with a shoulder at 400 eV was attributed to different C-N bonding (C=N and C-N). Hence it is believed that the carbon coating formed around the alloy particles during the heat treatment at 900°C has a graphitic-like structure containing some nitrogen atoms. Nitrogen incorporation into graphene layer is responsible for the curvature of the graphitic planes resulting in encapsulation. The carbon coating of the nanoparticles prepared according to the precipitation method contains 7 surface atom % of nitrogen that may make these encapsulated particles fundamentally and structurally different from the ones produced by the Geus method whose carbon jacket contains only carbon atoms and hence is made up of essentially planar plates.

Magnetic properties

Figure 9 shows the experimentally measured saturation magnetization of a typical spray-precipitation-pyrolysis sample. The material exhibits a saturation magnetization of 110 emu per gram mass of the sample at $>8 \times 10^4$ A/m (>1000 Oersted). We estimate from the TG experiments (not shown) that this typical carbon encapsulated nano-alloy sample contains 67% alloy content. Thus taking account of the alloy content which mainly contributes to the magnetization (the graphite jacket is thought to contribute insignificantly as compared to the central soft magnetic Fe-Ni alloy core), the saturation magnetization of this material per gram of alloy would be 165 emu/g. Literature value of bulk nickel-iron alloys of Ni:Fe ratio of 1.0 indicates 156 emu/g. Hence, within experimental error the present encapsulated alloy material appears to display a similar saturation magnetization to that of the bulk alloy. Table 1 summarises the comparison of the saturation magnetization values displayed by the spray-precipitation-pyrolysis sample with the literature values using the alumina-supported alloy particles with and without acid treatment.

Table 1. The normalised saturation magnetization values per gram of Fe-Ni alloy in the two samples

Sample	After encapsulation			After HCl treatment	
	Alloy content (wt%)	Ms (emu/g)	Hc (Oe) *	Ms (emu/g)	Hc (Oe)
Spray-precipitation-pyrolysis	67%	165	1000	105 (8 hrs)	1000
Alumina-supported alloy	18.8%	130	100	48 (30 mins)	50

* 1 Oe = 80 A/m

It is noted from the Table 1 that the slightly lower saturation magnetization of the Ni-Fe alloy on alumina (130 emu/g) of the Geus particles could be due to an incomplete reduction of metal oxides to alloy. Because of the much higher alloy content in the spray-precipitation-pyrolysis sample than Geus sample it displays a higher saturation magnetization value per gram of sample mass (110 vs 24.4). It is interesting to find that the saturation magnetization decreases when samples are treated with acid (36% decrease in the spray sample vs 63% in the alumina sample). It is believed that the decrease in saturation magnetization is caused by dissolution of alloy particles which have not been fully encapsulated by carbon layers. Hence, we believe that a larger quantity of fully encapsulated particles is made using the spray-precipitation pyrolysis technique whereby the impermeable graphitic layers offer a total protection to the encapsulated nanoparticles against leaching in the strong acidic environment. On the other hand, the Geus method does not provide a full protection of its encapsulated particles against acid treatment. Notice that the removal of alumina support would require acid treatment in order to release the carbon encapsulated Fe-Ni particles. It is however not entirely necessary for

the spray samples where no support material is present. Even without acid treatment the present samples can equally disperse in aqueous medium very well as a colloid and without any significant attenuation in their saturation magnetization when the samples are pre-treated with a bleach solution (mild oxidation to introduce surface functionalities - such as phenolic and carboxylic groups on the carbon surface) at pH 9. These surface groups with different ϵ surface potentials provide anchoring points for catalyst (homogeneous or heterogeneous) immobilisation. At different pH, they also play a significant role for the particle dispersion or flocculation in the solvent.

15 Catalytic action

Figure 10 shows the 5% Pd impregnated spray-precipitation-pyrolysis sample is an active catalyst for the hydrogenation of nitrobenzene to aniline. Table 2 shows the comparison of the initial rate of reaction (extrapolation to time zero) of this material with a commercial Pd/C catalyst.

Table 2 showing the initial rates of nitrobenzene hydrogenation over two Pd samples

Catalyst	Initial rate (μ -mole of nitrobenzene converted to aniline s^{-1})
5% Pd/spray-precipitation-pyrolysis sample	1.529 (32 mg catalyst)
5% Pd/C (a commercial catalyst)	0.835 (50 mg catalyst)

It is found that the present catalyst shows almost double the rate of hydrogenation compared to a commercial catalyst with the same metal loading. We attribute the higher activity of the Pd doped spray sample of the

invention in nitrobenzene hydrogenation to the better Pd dispersion onto the nano-size carbon particles (colloidally dispersed in the solvent) as compared to the micro-size commercial catalyst powder. The flocculation of the nano-size magnetic catalyst particles is easily achieved by applying an external magnetic field, which facilitates its filtration from the product solution.

In general, premature clustering of ferromagnetic particles can be prevented by using soft ferromagnetic materials in which the remnant magnetic moment (the magnetic moment in the absence of a magnetic field) is low. The measured 110 emu per gram of the present (the saturation magnetization is greater than pure iron particles) allows effective precipitation (separation) or re-dispersion of the particles in liquid phase by simply switching the external magnetic field on or off. The magnetic interaction between magnetic particles can be modulated by the application of 'spacer' materials between the magnetic particles such as the number of carbon shells and the background amorphous carbon. By changing the relative concentration of the metal complexes and carbon sources (polymer + ligands) or changing the droplet size (using different spray heads) the overall magnetic properties of these particles can be finely tuned.

Synthesis Examples 8 to 20

The procedure of Synthesis Example 2 was followed, omitting the solution of polyvinyl alcohol, and with variations of the pyrolysis conditions as set out in Table 3 below. Table 3 also gives the particle size of the Fe-Ni alloy cores formed in the graphitic shells of the particles formed.

Table 3

Example	Gas	Flow rate (ml/min)	Temp rise (°C/min)	Max. temp. (°C)	Time at Max. temp. (h)	Core particle size (nm)
8	N ₂	100	10	900	10	44.7
9	N ₂	100	10	900	16.5	35.8
10	N ₂	100	1	900	10	29.0
11	N ₂	600	1	900	10	27.7
12	N ₂	15	1	900	10	26.4
13	Ar	100	10	900	10	39.0
14	Ar	100	10	900	10	37.5
15	N ₂	1000	10	900	10	24.0
16	Ar	1000	1	900	10	23.8
17	Ar	1000	10	600	10	14.3
18	Ar	1000	1	600	10	14.3
19	Ar	1000	1	900	6 min.	24.2
20	Ar	1000	20	900	6 min.	-

- not measured

It can be seen that a lower temperature increase rate, a lower maximum temperature and a higher gas flow rate contribute to smaller core size.

Synthesis Examples 21 to 28

The procedure of Synthesis Example 2 was again followed, omitting the solution of polyvinyl alcohol, using different pairs of metal precursors, as shown in Table 4. The amounts of the precursors are chosen to aim at a metal/metal atomic ratio of 1:1 or 2:1. In Examples 21 to 25 ammonia solution was employed for precipitation as in Example 2, but in Examples 26 to 28 a very slightly alkaline solution (NaOH) was used instead. Table 4 also shows the atomic ratios of the elements in the precipitated particles before their pyrolysis and the size of the Fe-Ni alloy core after pyrolysis.

Table 4 shows that the use of a sulphur-containing ligand in Example 24 apparently inhibited the graphite shell formation, leading to a larger sintered core

particle size. Analysis data indicated that in all Examples the complete decomposition of the cyanide groups, the metal reduction and alloy formation and carbon recrystallization all occurred below 600°C. XRD
5 indicated that Fe-Ni alloy is formed and that Fe and Ni metals are absent (in accordance with the Fe/Ni phase diagram for the conditions employed).

Table 4

Example	Metal cyanide precursor	2nd metal precursor	Atomic ratios			Core size (nm)
			Ni/Fe	C/Fe	C/Ni	
21	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.92	5.15	2.68	23.8
22	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.57	5.66	3.60	24.8
23	$(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.94	5.76	2.97	24.6
24	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Ni}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	1.98	4.77	2.41	58.3
25	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	1.84	4.97	2.70	22.2
26	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.00	4.92	4.94	22.0
27	$\text{K}_3\text{Fe}(\text{CN})_6$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.97	5.08	5.25	18.5
28	$\text{K}_2\text{Ni}(\text{CN})_4 \cdot x\text{H}_2\text{O}$	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0.97	3.66	3.73	43.5

Synthesis Example 29

Here the procedure of Synthesis Example 2 (omitting the polyvinyl alcohol solution) was modified to enable formation of a Fe-Co alloy core. The maximum
5 temperature was raised to 1000°C, to achieve alloy formation, in accordance with the Fe/Co phase diagram which indicate that 985°C is the minimum temperature for formation of the Fe-Co phase. Slightly alkaline solution (NaOH) was used for precipitation. Data for
10 this Example are:-

Metal cyanide precursor : $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$

Second metal precursor : $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Atomic ratios of precipitated particles

15 Co/Fe : 1.04

C/Fe : 5.13

C/Co : 4.93

N/C : 1.22

Core particle size : 49.1 nm

20

Synthesis Examples 30 to 32

Table 5 shows details of syntheses of carbon-encapsulated particles in which Fe and Zn are the metals. The procedure was in accordance with Synthesis
25 Example 2 (omitting the polyvinyl alcohol solution) except that in Example 32 slightly alkaline NaOH was employed instead of ammonia solution. The calcining temperature was 900°C for 10 hours as in Example 2. Analysis of the particles produced showed that the
30 predominant phase in the core is Fe_3C , with some peaks in XRD corresponding to $\text{Zn}(\text{CN})_2$ and some possible traces corresponding to Fe-Zn alloy. The core is

ferromagnetic. This segregation to carbide, rather than alloy formation, presumably is thermodynamically favoured.

5 Table 5

Example	Iron precursor	Zinc precursor	Atomic ratios*			
			Zn/Fe	C/Fe	C/Zn	N/C
30	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.71	4.57	2.67	1.56
31	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.44	5.42	3.77	1.52
32	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.99	5.03	5.08	1.16

* analysis of precipitate before pyrolysis

Synthesis Examples 33 to 35

Carbide formation in the core was also observed
 10 when Fe and Mn were the metals. Details are given in Table 6.

Table 6

Example	Iron precursor	Manganese precursor	Atomic ratios*				Size (nm)
			Mn/Fe	C/Fe	C/Mn	N/C	
33	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.66	5.00	1.90	1.45	93.6
34	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.42	6.70	2.76	1.47	-
35	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1.03	4.97	4.81	1.16	-

- = not measured. * analysis of precipitate before pyrolysis

15

The procedure was as in Example 2, omitting the polyvinyl alcohol solution. In Example 35, the NaOH solution was used for precipitation.

In analysis, EDX showed a good signal of the Fe and
 20 Mn after the sample was calcined. Excellent carbon encapsulation of cores containing Fe and Mn within graphitic shells were shown by the TEM micrographs. XRD on the other hand, indicated that the predominant phases were Mn_5C_2 and FeC_3 (or Fe_7C_3) with some minor phases

which appeared to match with FeMn_4 (alloy). It is noted that a phase diagram of Fe and Mn suggests that they should form alloy under the conditions. However, in the presence of carbon atoms, phase segregation to their carbides was clearly evident under the reaction temperatures. The particles are ferromagnetic.

Synthesis Examples 36 - 39

Using $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ as the iron precursor, the procedure of Example 2 (omitting polyvinyl alcohol solution) was performed using Ca salts as a second metal precursor (alone or in combination with Ni). Compare Example 4 above. The materials, ICP (Inductive Couple Plasma) data, calcining gas and XRP results are shown in Table 7.

Table 7

Example	2nd metal precursor	ICP (wt%)			Cal. gas	Phase	XRD Size (nm)
		Fe	Ni	Ca			
36	Ca(NO ₃) ₂ ·4H ₂ O	16.60	0.00	-	N ₂	Ca(CN) ₂ +Fe ₃ C+Fe	33.9
37	CaCl ₂	14.40	0.00	17.00	N ₂	Ca(CN) ₂ +Fe+Fe ₃ C	-
38	CaSO ₄	5.79	0.00	21.40	N ₂	CaS+Ca ₂ Fe ₂ O ₅ +CaO	-
39	Ni(NO ₃) ₂ ·6H ₂ O/Ca(NO ₃) ₂ ·4H ₂ O	13.00	12.60	-	Ar	FeNi+Ca(CN) ₂	25.8

- = not measured

As discussed in Example 4, no known alloy phase of Fe-Ca is previously reported. In this particular case, characterisations (XRD, TEM, FTIR, EDX) were carried out after calcination (before and after acid treatment).

5 Before the acid treatment it was interesting to find that the dominant phases were FeC_3 (25-33nm), Fe and $\text{Ca}(\text{CN})_2$ (EDX showed a high concentration of Ca and FTIR indicated the CN structure). After the acid treatment the Ca content and $\text{Ca}(\text{CN})_2$ phase were significantly
10 attenuated but the Fe carbide and Fe phases remained unchanged. This clearly suggests that some Ca phases were apparently not protected by the graphitic shells. Presumably the carbon encapsulation was only initiated by the iron since no alloy was present.

15

Synthetic Examples 40 to 44

Carbon-coated Fe-Cu particles were obtained. Precursor materials and results are given in Table 8. The procedure of Example 2 (omitting polyvinyl alcohol
20 solution) was followed, except that the NaOH solution was employed in Examples 43 and 44. The two core sizes relate to the Fe and Cu phases respectively.

Table 8

Example	Iron precursor	Copper precursor	Atomic ratios*			Size (nm)
			Cu/Fe	C/Fe	C/Cu	N/C
40	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1.02	3.68	3.62	1.32
41	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	3.34	4.36	1.31	3.01
42	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Cu}(\text{CH}_3\text{COO})_2$	-	-	-	-
43	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1.04	5.01	4.78	1.24
44	$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	1.00	4.04	4.03	1.14

* analysis of precipitate before pyrolysis - = not measured

-

33.7/80.4

46.8/88.0

-

According to the chemical analyses Fe-Cu (1:1) species can be selectively precipitated by using ammonia or NaOH. The TEM produced a clear evidence of particle encapsulation within graphitic shells. On the other
5 hand, XRD indicated separated Fe and Cu phases (33.7 nm Fe, 80.4 nm Cu), despite the fact that formation of Fe-Cu alloy was predicted (no carbide phases were derived).

Synthetic Examples 45 and 46

10 Table 9 gives data for two further examples where ferromagnetic alloy cores not containing Fe were encapsulated in graphitic shells, using the method of Example 2 (omitting polyvinyl alcohol solution).

Table 9

Example	Metal cyanide precursor (1)	2nd metal precursor (2)	Molar ratios			N/C	phase	XRD size
45	$K_2Ni(CN)_4 \cdot xH_2O$	$Co(NO_3)_2 \cdot 6H_2O$	1.1	2.7	2.5	1.5	NiCo	120.6
46	$K_2Pt(CN)_4 \cdot 3H_2O$	$Co(NO_3)_2 \cdot 6H_2O$	1.0	3.7	3.7	1.1	CoPt	21.0

* analysis of precipitate before pyrolysis

Example 47 - Magnetic property

Figure 9 discussed above shows magnetization properties of one example of particles of the present invention. Fig. 19 shows the magnetic responses, obtained in the same manner, for other graphite encapsulated magnetic particles (containing metal, alloy, carbide or mixtures) obtained as described above. The components are Fe-Ni (as in Fig. 9), Fe/Ca (probably Fe₃C phase), Fe-Cu, Fe/Mn (carbides), Fe/Zn (carbides), Fe-Co.

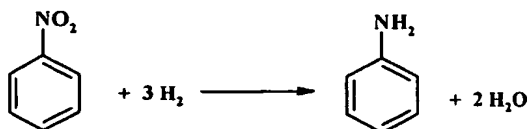
It is shown that these carbon protected magnetic particles all displayed no magnetic hysteresis (a high magnetisation response but with no magnetic aggregation of the fine particles in solution in the absence of non-homogenous magnetic field). Hence they are well suited as magnetic catalyst particles. It has been demonstrated that these fine particles can be magnetically precipitated under non-uniform magnetic field and be re-dispersed in the absence of magnetic field (with stir).

Example 48 - Catalysis

Additional catalytic results are given in Fig. 20, for

furnace carbon black treated with HCl	(◇)
particles of Example 2, before acid treatment	(□)
particles of Example 2 treated with HCl	(◆)
particles of Example 2 treated with HCl and carrying Pd	(■)

Hydrogenation of nitrobenzene



300ml batch stainless steel Parr reactor:

Substrate: nitrobenzene (6.5 ml)

Solvent: isopropanol (IPA, 125.0 ml)

5 Catalyst 12 mg.

Purges: flowing N₂ (ambient pressure/15 minutes)

+ pure H₂ (20 bar/3 times).

Stirring (560 rpm), pressure (H₂, 40 bar),

temperature (80°C), time (6 h).

10

The particles having noble metal (Pd) at the surface rapidly catalyse hydrogenation of nitrobenzene at a much faster rate than the reaction catalysed by the acid sites on carbon surface. In our study, HCl treatment was used to remove the unprotected metal or alloy from the carbon coated Fe-Ni sample. From the figure the activity for the HCl treated carbon encapsulated magnetic Fe-Ni phase was shown to be comparable to the HCl-treated furnace carbon black (a low activity). It was shown clearly the Pd deposited onto these magnetic carbon composites can be used as an excellent Pd supported catalyst for the reaction. It was clearly demonstrated that these fine composite catalyst particles can be magnetically precipitated when the non-uniform magnetic field was applied.

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CLAIMS

1. A method of forming microparticles with a ferromagnetic core encapsulated in a graphitic shell containing hetero atoms, which includes the steps of providing a solution containing source material of a ferromagnetic metal, carbon and the hetero atoms, forming solidified particles containing source material of the ferromagnetic metal, carbon and the hetero atoms from said solution, and pyrolysing said solidified particles in inert gas so as to form said ferromagnetic core and said encapsulating graphitic coating containing hetero atoms.

2. A method according to claim 1, wherein the solution is divided into droplets prior to forming of the solidified particles.

3. A method according to claim 2, wherein the solidification is carried out by precipitation of the droplets.

4. A method according to claim 2, wherein the solidification is carried out by injection of the droplets into the pyrolysis zone.

5. A method according to claim 1, wherein the solidified particles are formed by chemical precipitation in bulk in said solution.

6. A method according to any one of the preceding claims, wherein the hetero atoms are at least one of N, B, P or O.

7. A method according to any one of the preceding claims wherein the solution contains at least one of a metal cyanide compound, a metal isocyanide compound, a metal cyanate compound and a metal isocyanate.

8. A method according to claim 7 wherein said compound contains a complex anion selected from metal cyanide, metal isocyanide, metal cyanate and metal isocyanate complex anions.
- 5 9. A method according to any one of the preceding claims wherein the solution contains a cationic species containing or consisting of a first metal and an anionic species containing a second metal, the first and second metal being the same or different and at least one of the
- 10 10. A method according to claim 9 wherein each of the first and second metal are selected from Fe, Ni, Ca, Zn, Cu, Mn, Co, Mg, Pd, Pt, Ti, Mo and V.
11. A method according to any one of the preceding
- 15 11. A method according to any one of the preceding claims wherein the ferromagnetic core contains at least one metal in elemental or alloy form.
12. A method according to any one of the preceding claims wherein the ferromagnetic core contains at least one metal carbide.
- 20 13. A method according to any one of the preceding claims, wherein the solution additionally contains a diluent precursor which form a diluent for the pyrolysed particles.
14. A method according to claim 13, wherein the diluent
- 25 14. A method according to claim 13, wherein the diluent precursor is a decomposable carbon-containing compound which forms an amorphous matrix upon pyrolysis.
15. A method according to any one of the preceding claims including the step of treating the surface of the particles and/or the matrix to produce catalytic
- 30 activity.

16. A method according to claim 15, wherein the treatment includes deposition of a catalytically active metal.

5 17. Microparticles having a ferromagnetic core encapsulated by a graphitic curved shell containing hetero atoms.

18. Microparticles according to claim 17, wherein the curved shell is of a plurality of layers of graphite sheets.

10 19. Microparticles according to claim 17 or claim 18 wherein the core has a diameter in the range 5 to 500 nm, preferably 10 to 150 nm.

20. Microparticles according to claim 17, 18 or 19 which are embedded in an amorphous matrix.

15 21. Microparticles according to any one of claims 17 to 20 which have a catalytically-active surface.

22. Microparticles according to claim 20, wherein the matrix has a catalytically-active surface.

20 23. Microparticles according to claim 21 or 22, wherein the catalytic activity is due to a metal deposited on the surface.

24. Microparticles according to any one of claims 17 to 23 wherein the ferromagnetic core consists of at least one phase selected from metal, alloy, carbide and oxide.

25 25. Use of microparticles according to any one of claims 17 to 24 as catalyst in a liquid-phase reaction.

26. Use of microparticles made by the method of any one of claims 1 to 16 as catalyst in a liquid phase reaction.

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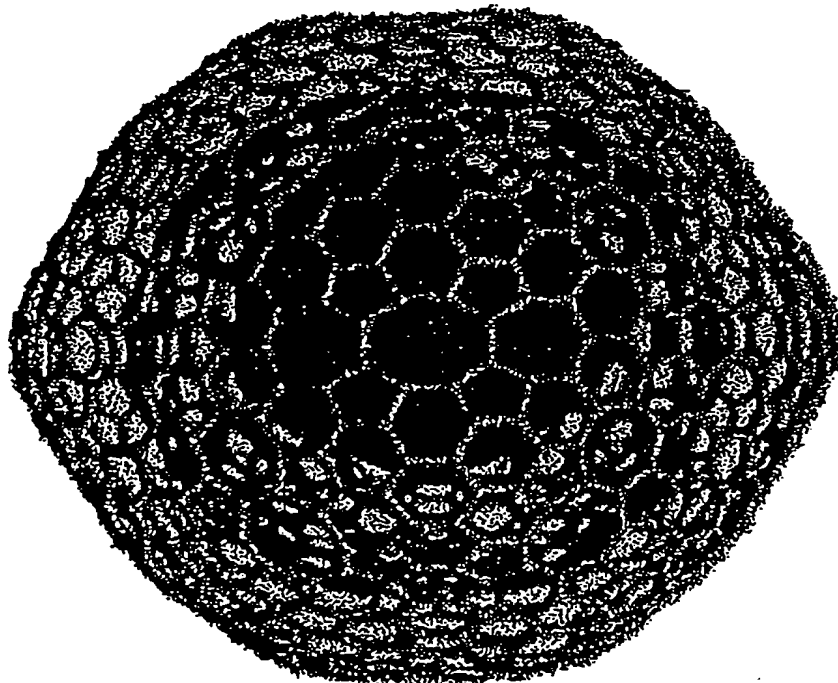


Fig. 1

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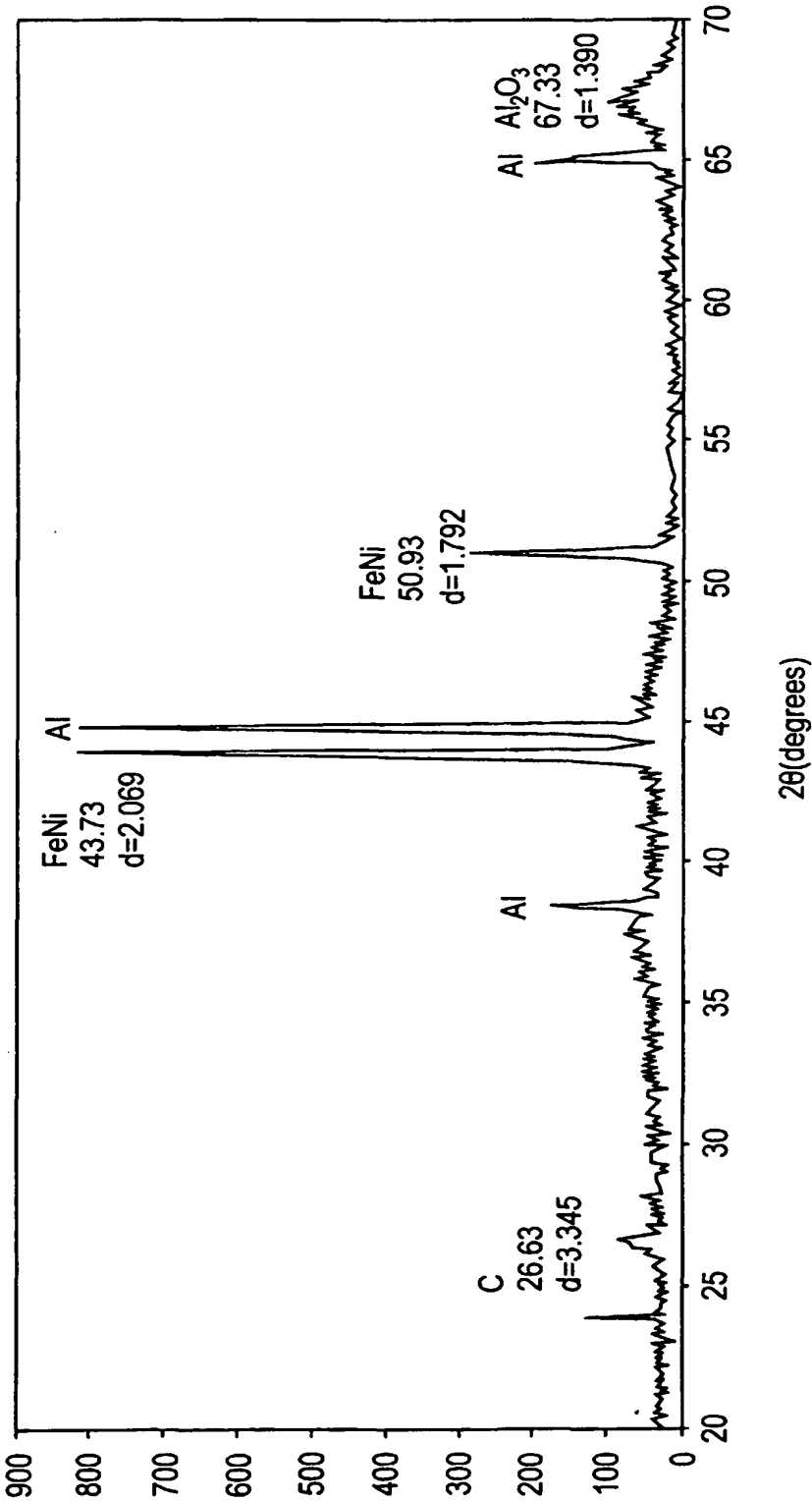


Fig. 2a

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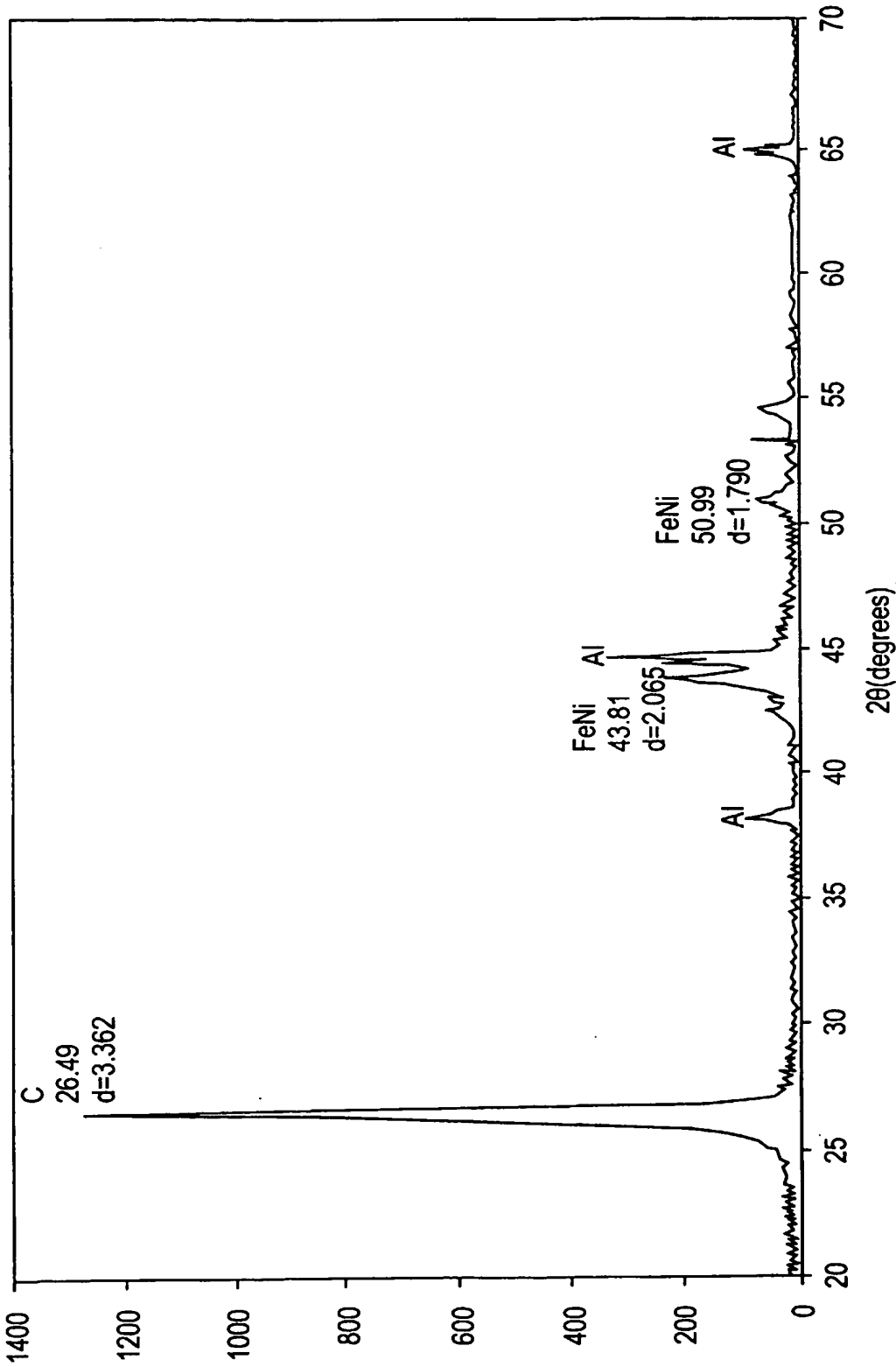


Fig. 2b

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Fig. 3

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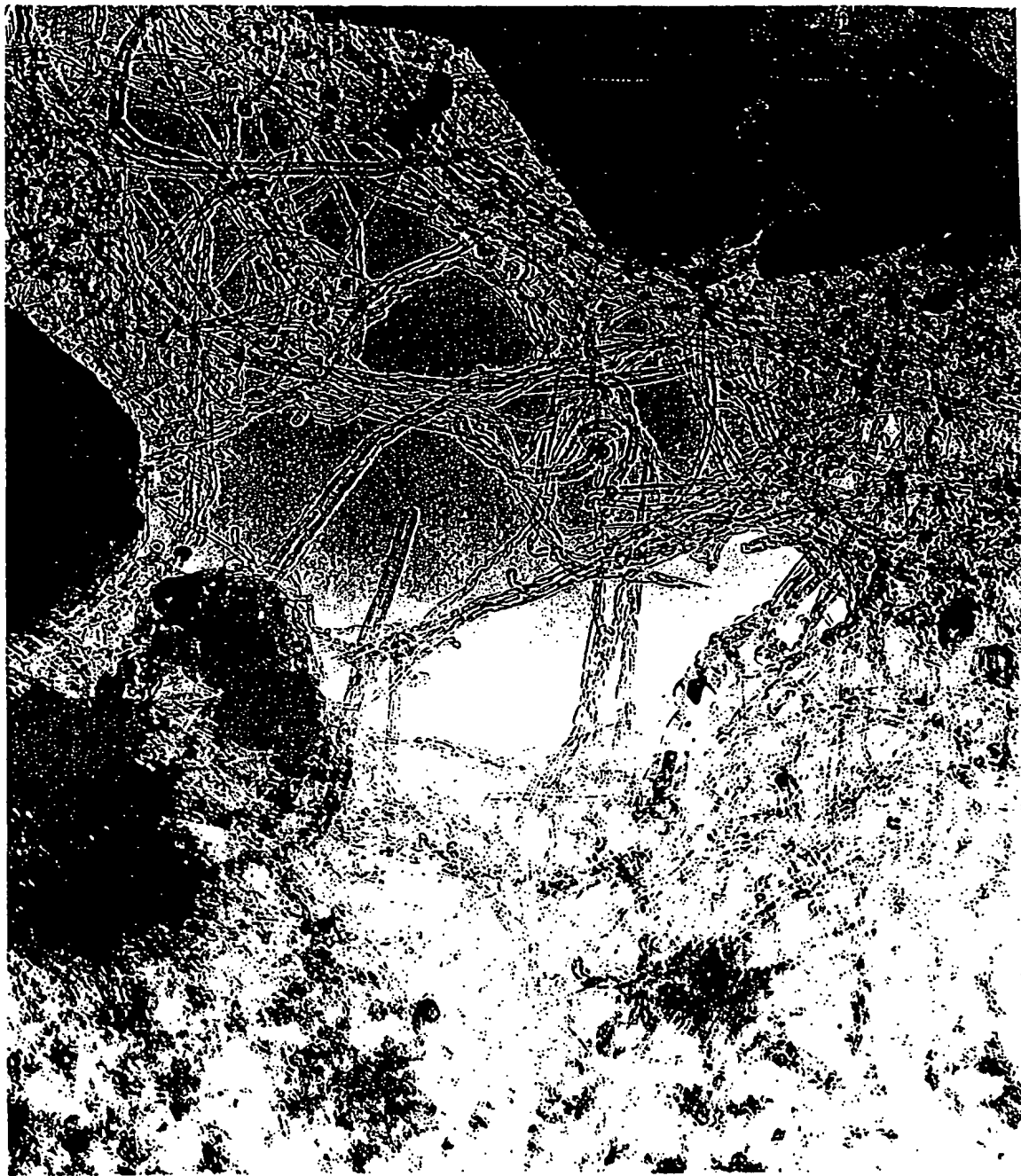
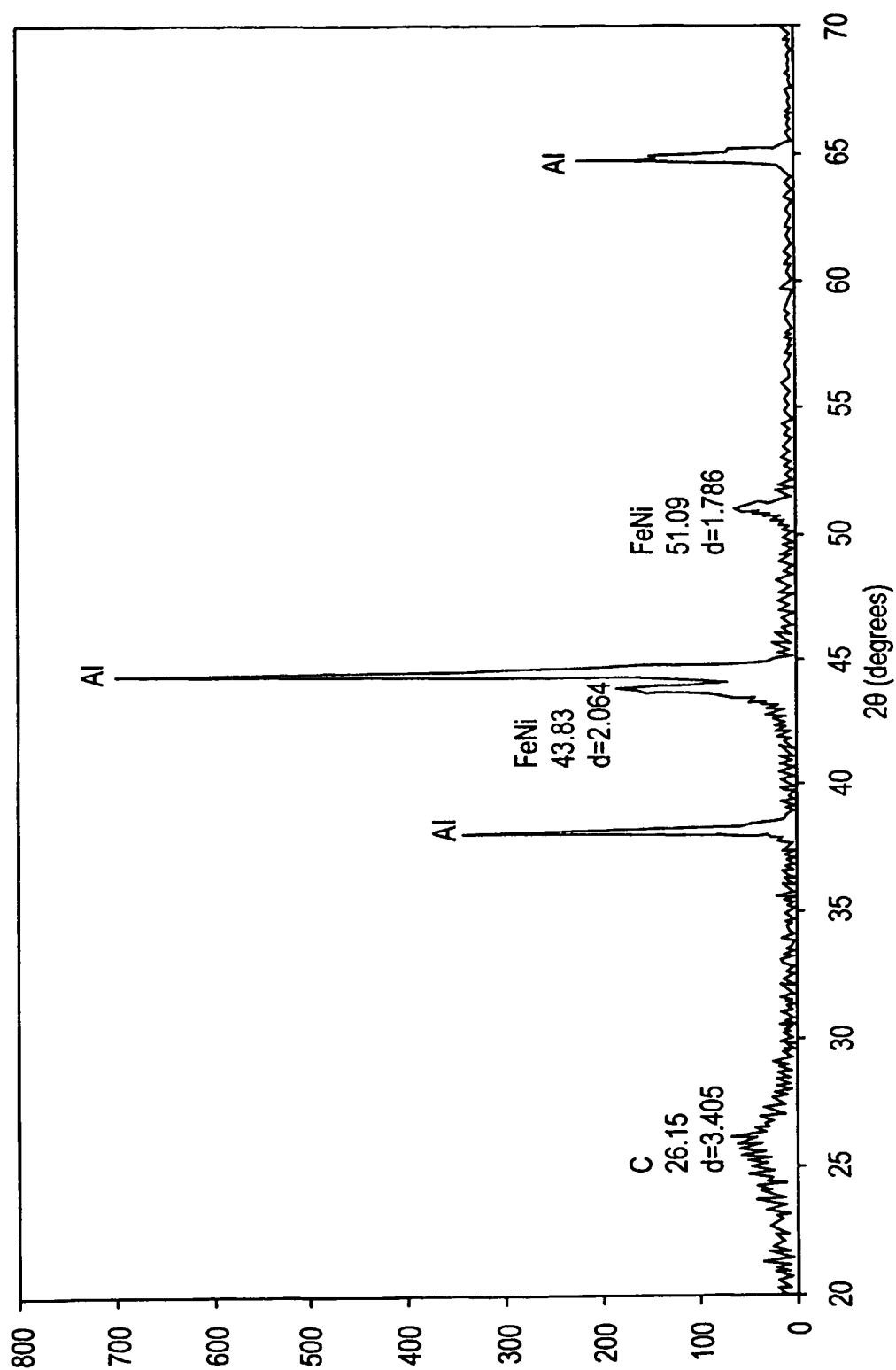


Fig. 4

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*Fig. 5*

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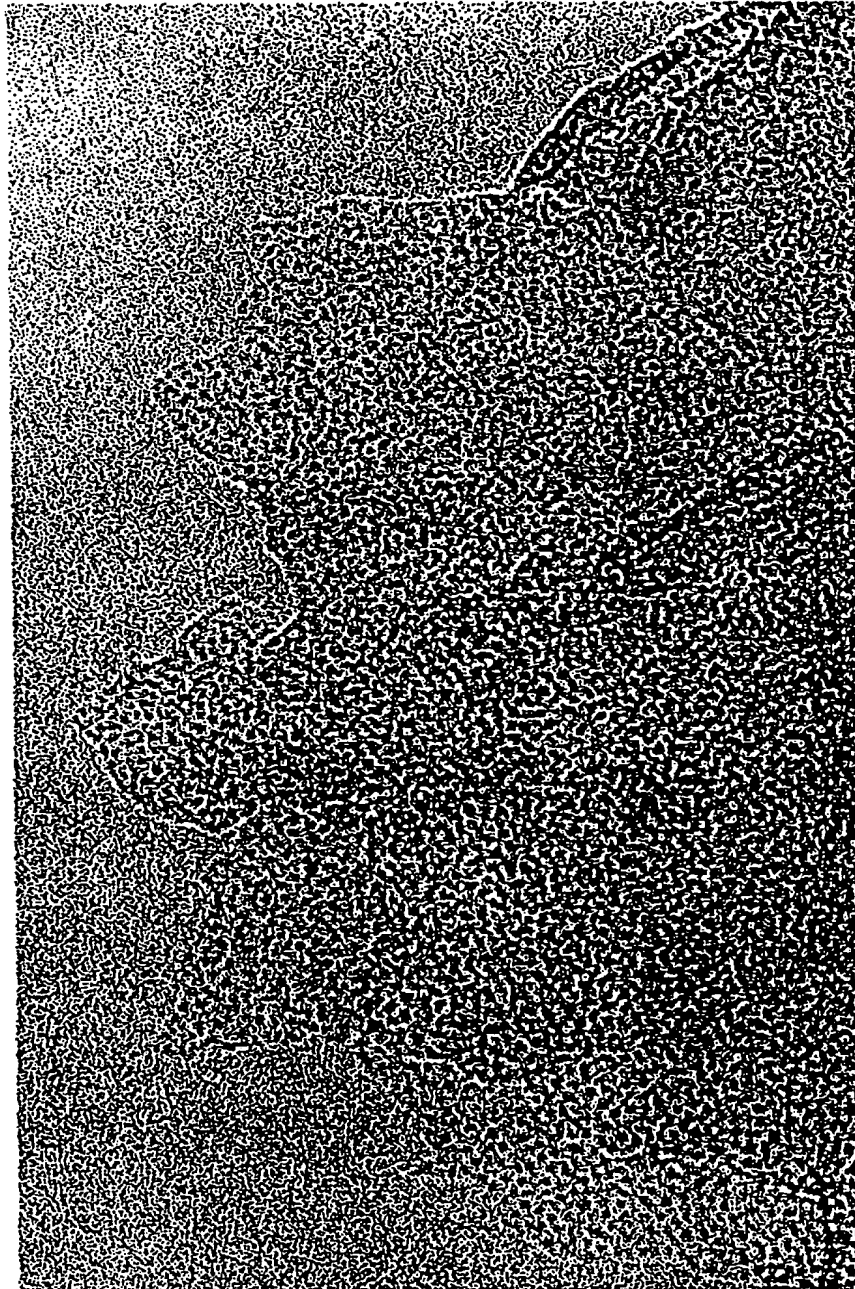


Fig. 6

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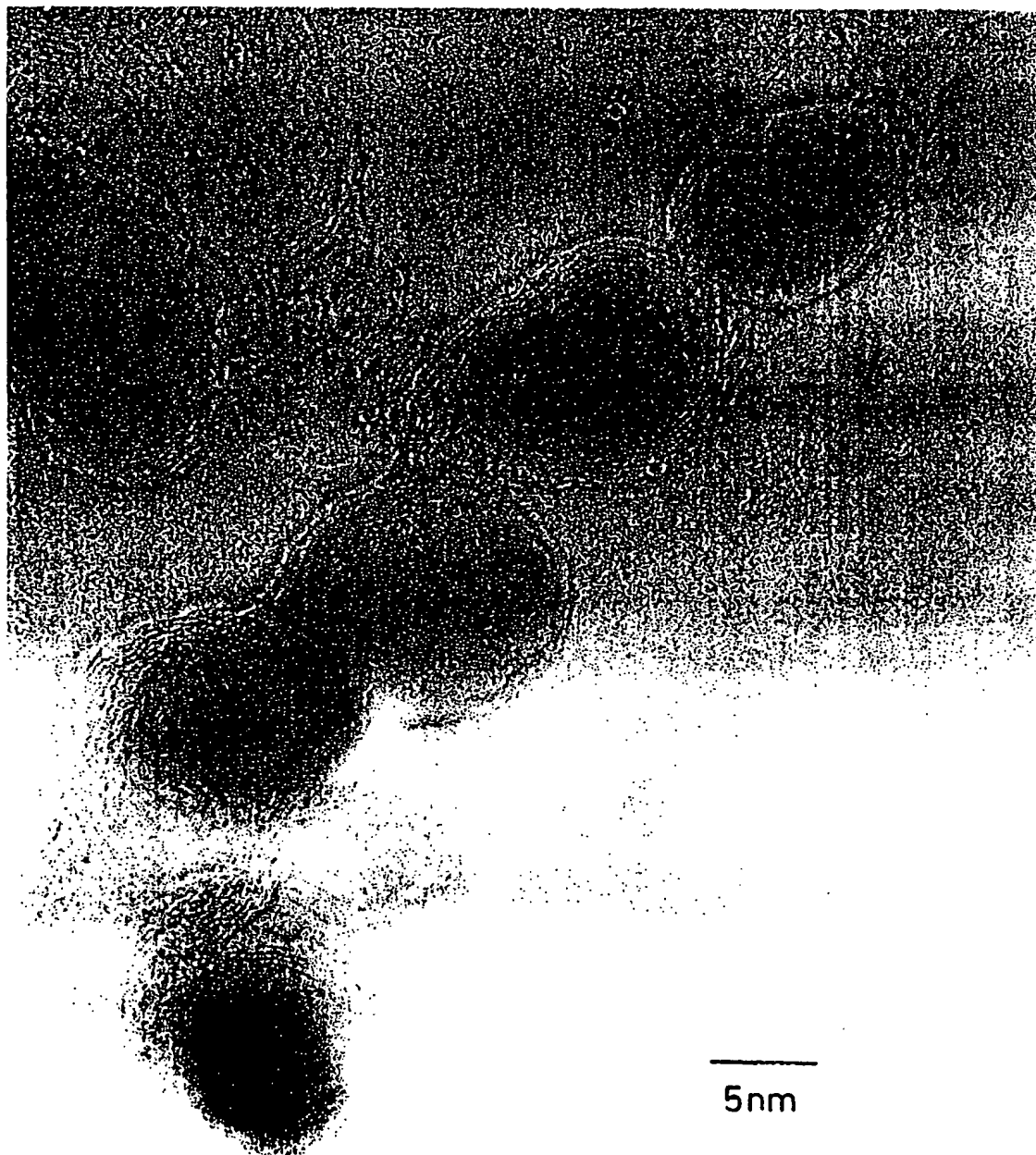
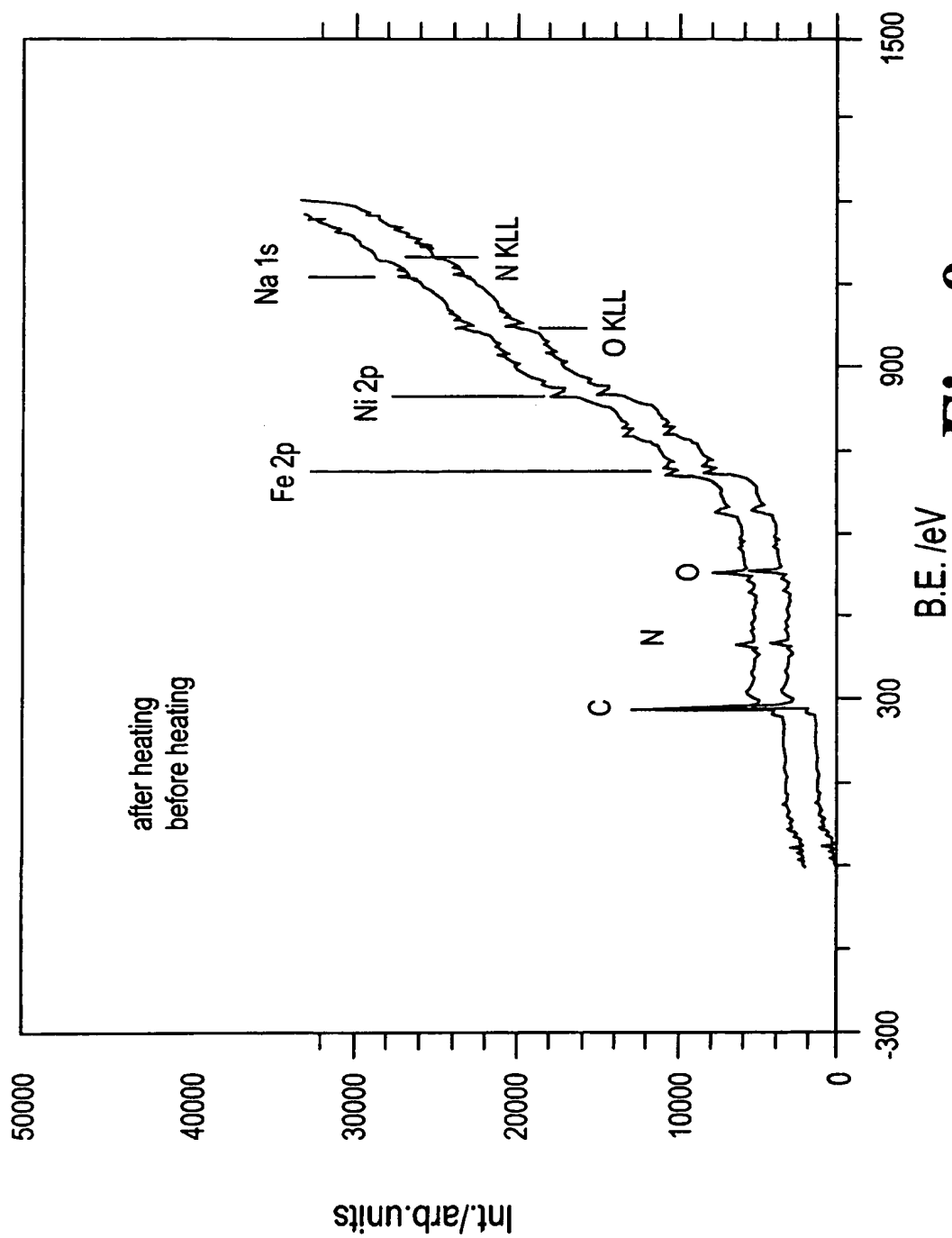


Fig. 7

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**Fig. 8a**

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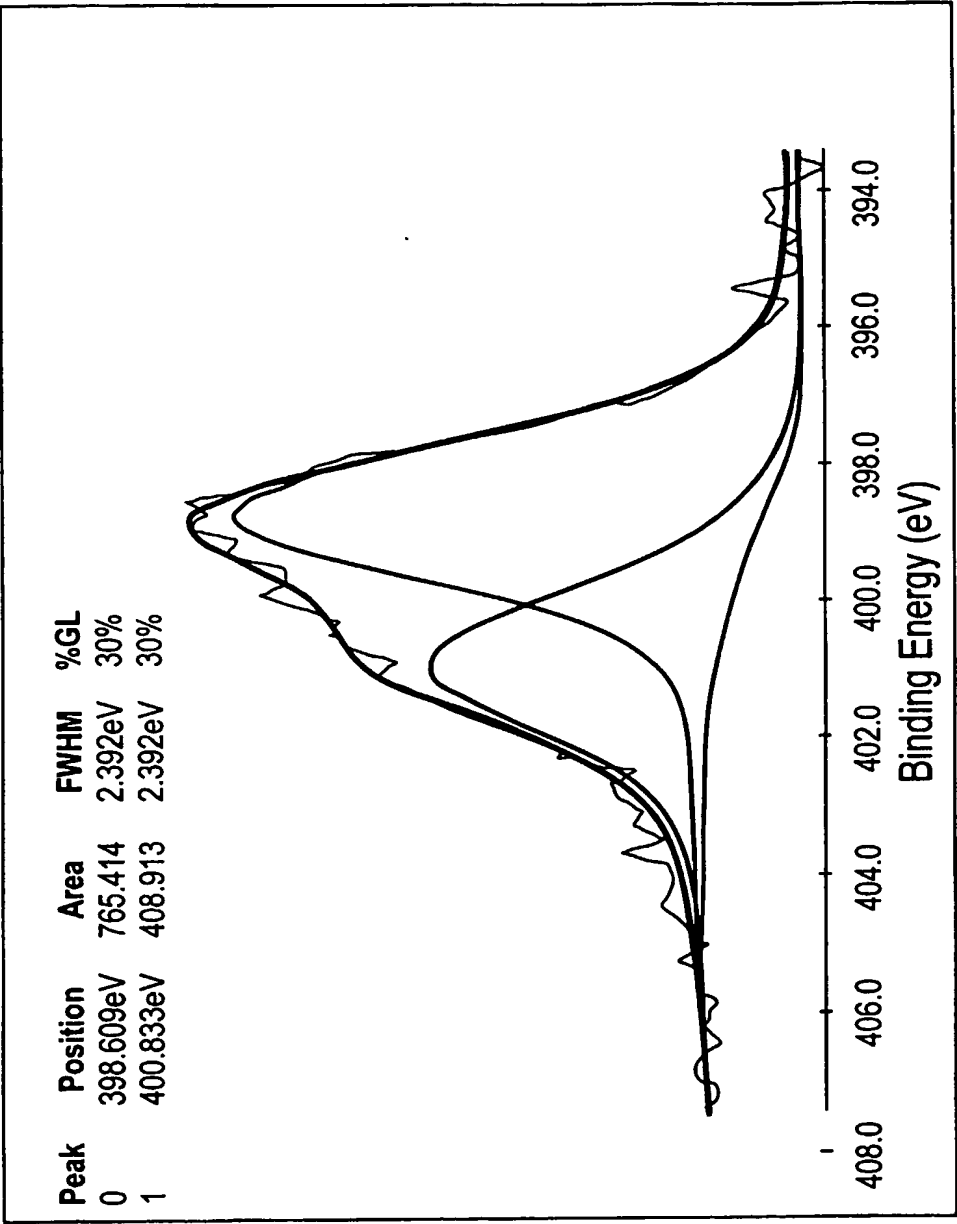


Fig. 8b

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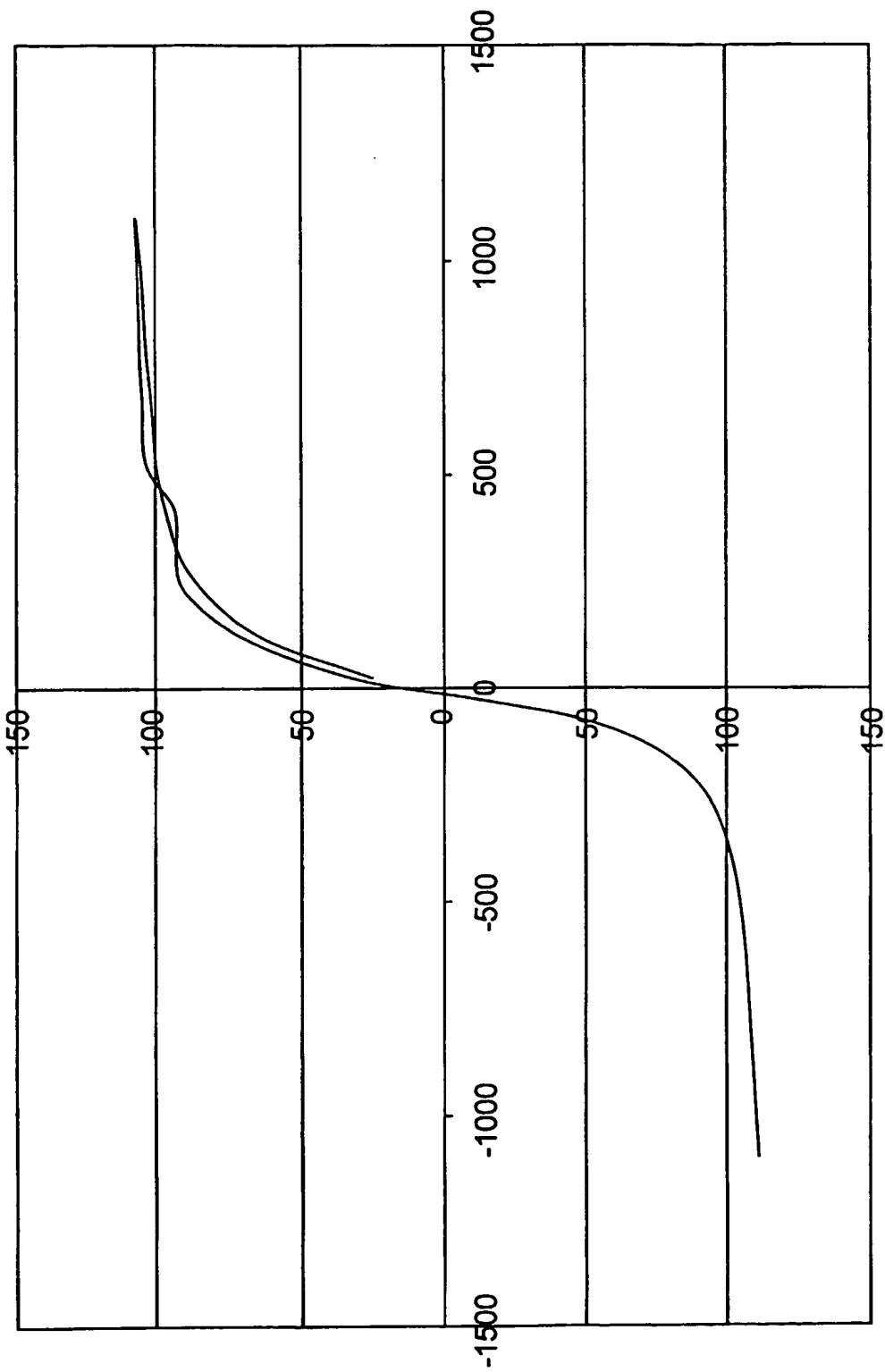
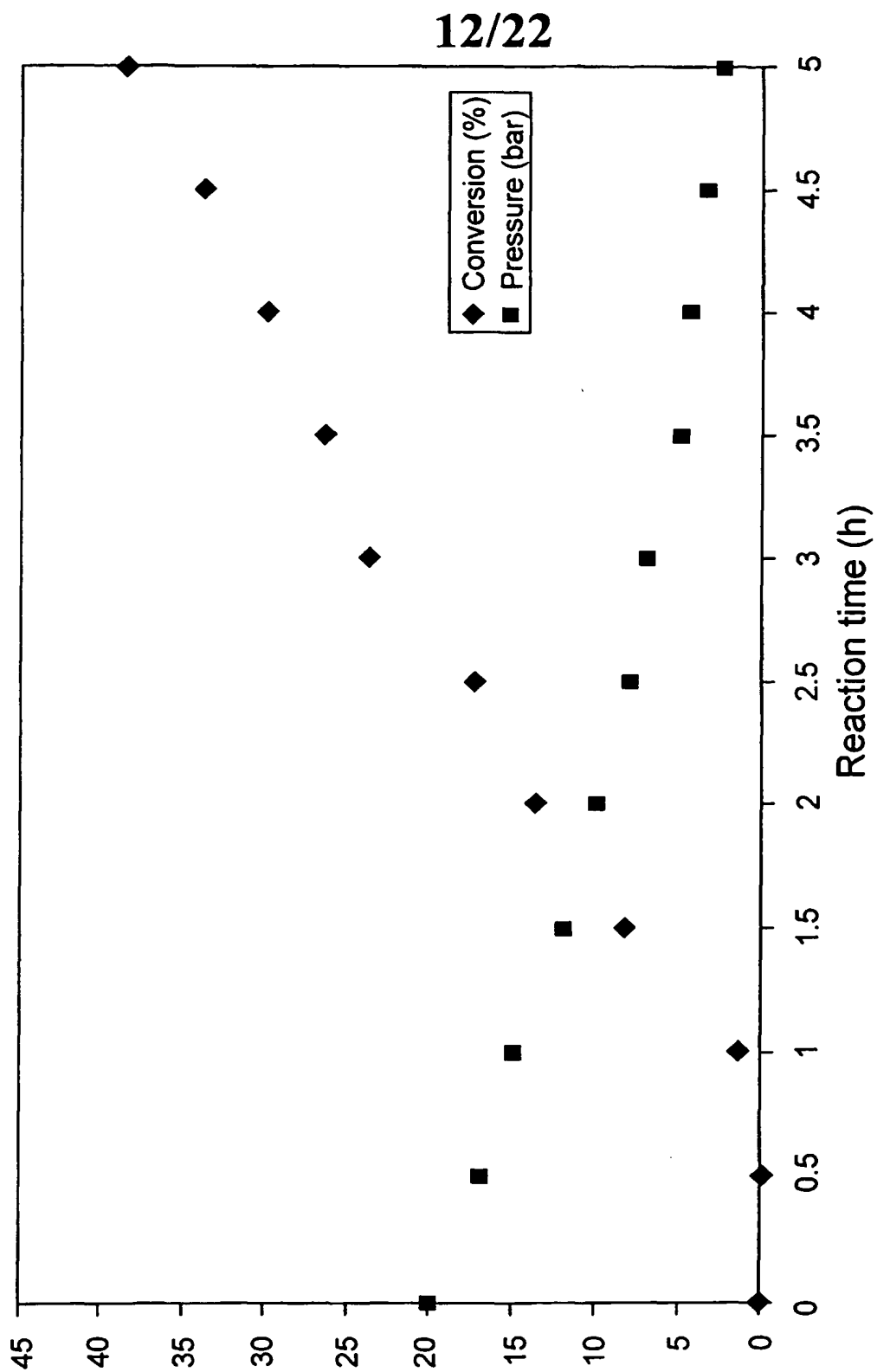


Fig. 9

*Fig. 10*

VC1

Lin (Counts)

2-Theta - Scale

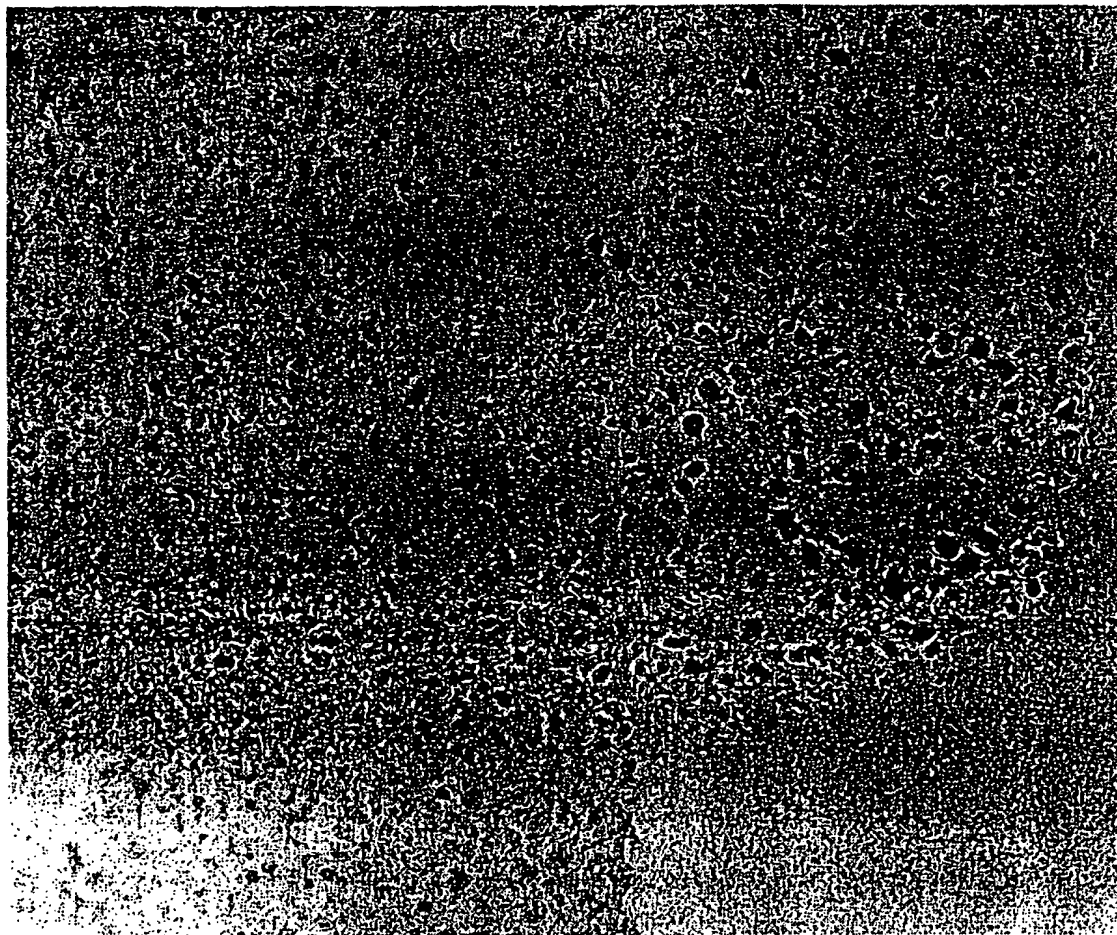
Fe

d=12.997
d=15.115
d=4.910
d=3.286
d=2.764
d=2.454
d=2.412
d=2.268
d=2.217
d=2.167
d=2.102
d=2.028
d=1.979
d=1.845
d=1.758
d=1.729
d=1.648
d=1.559
d=1.227
d=1.192
d=1.119
d=1.115
d=1.032
d=1.023
d=1.008

XRD spectrum of the FE/Ca system after calcination

Fig. 11

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TEM micrograph of the Fe/Ca system before calcinations (x 800,000)

Fig. 12

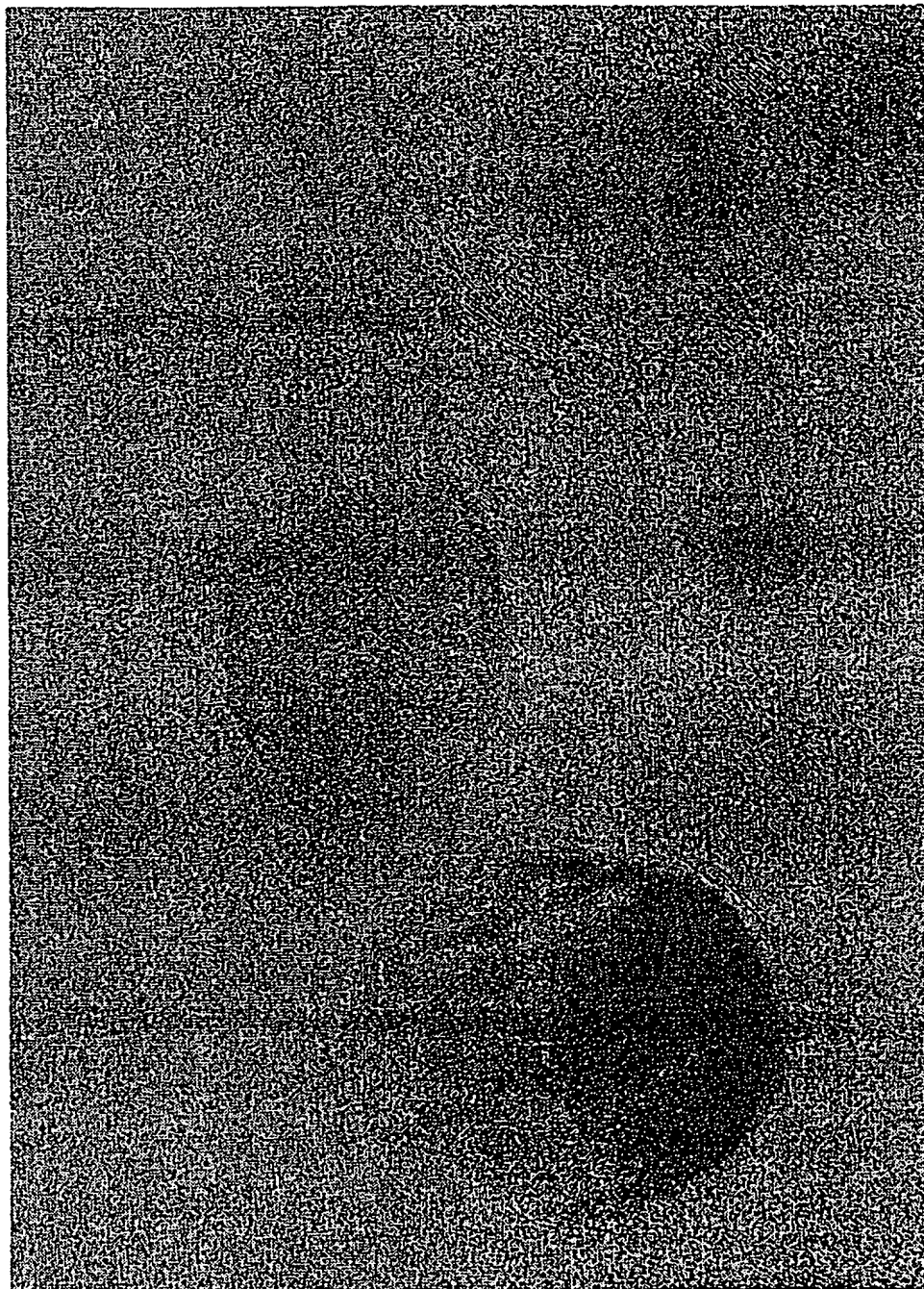
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Fig. 13

TEM micrograph of the Fe/Ca system after calcinations (x 60,000)

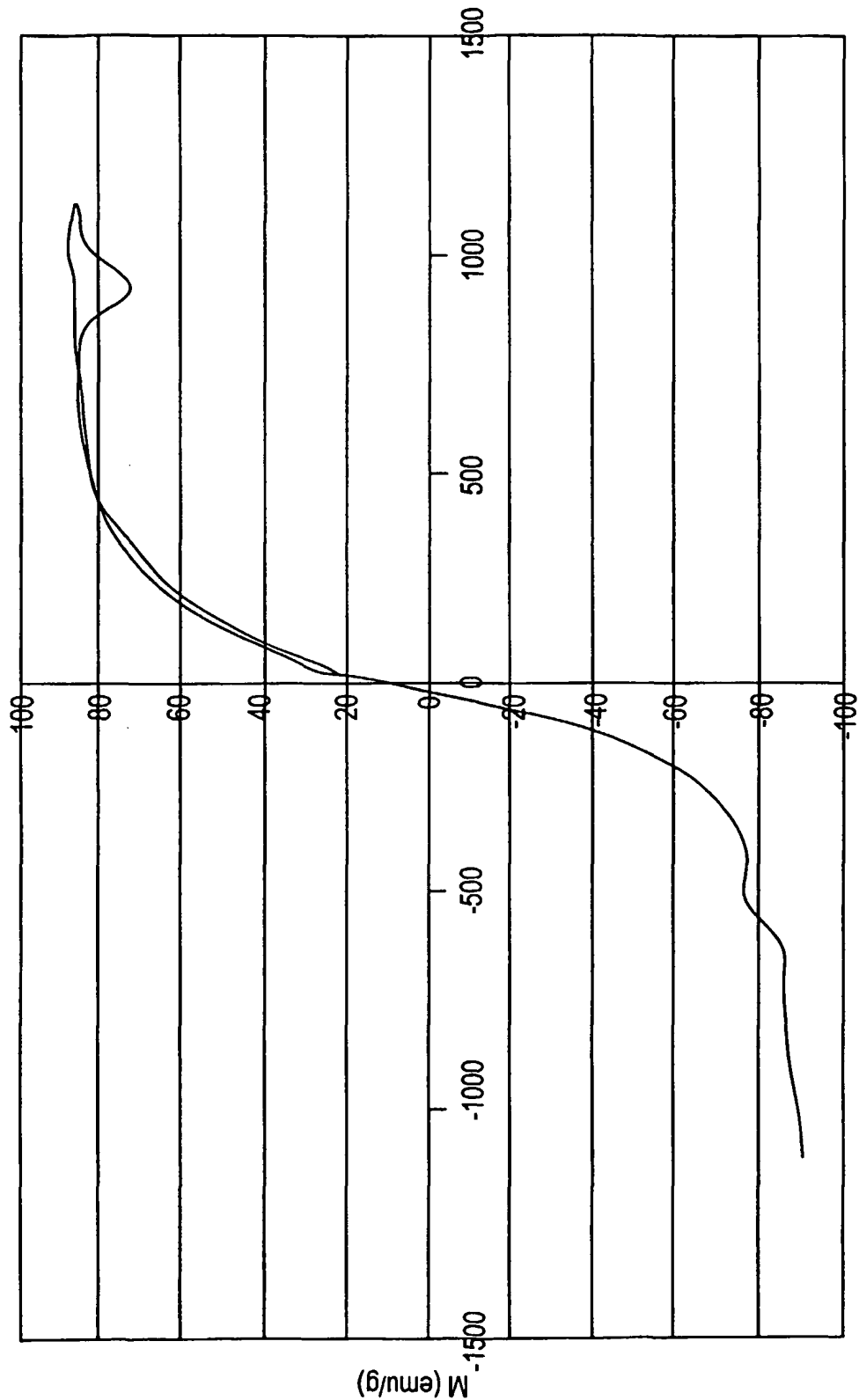
16/22



High resolution TEM micrograph of the Fe/Ca system after calcinations ($\times 1,240,000$)

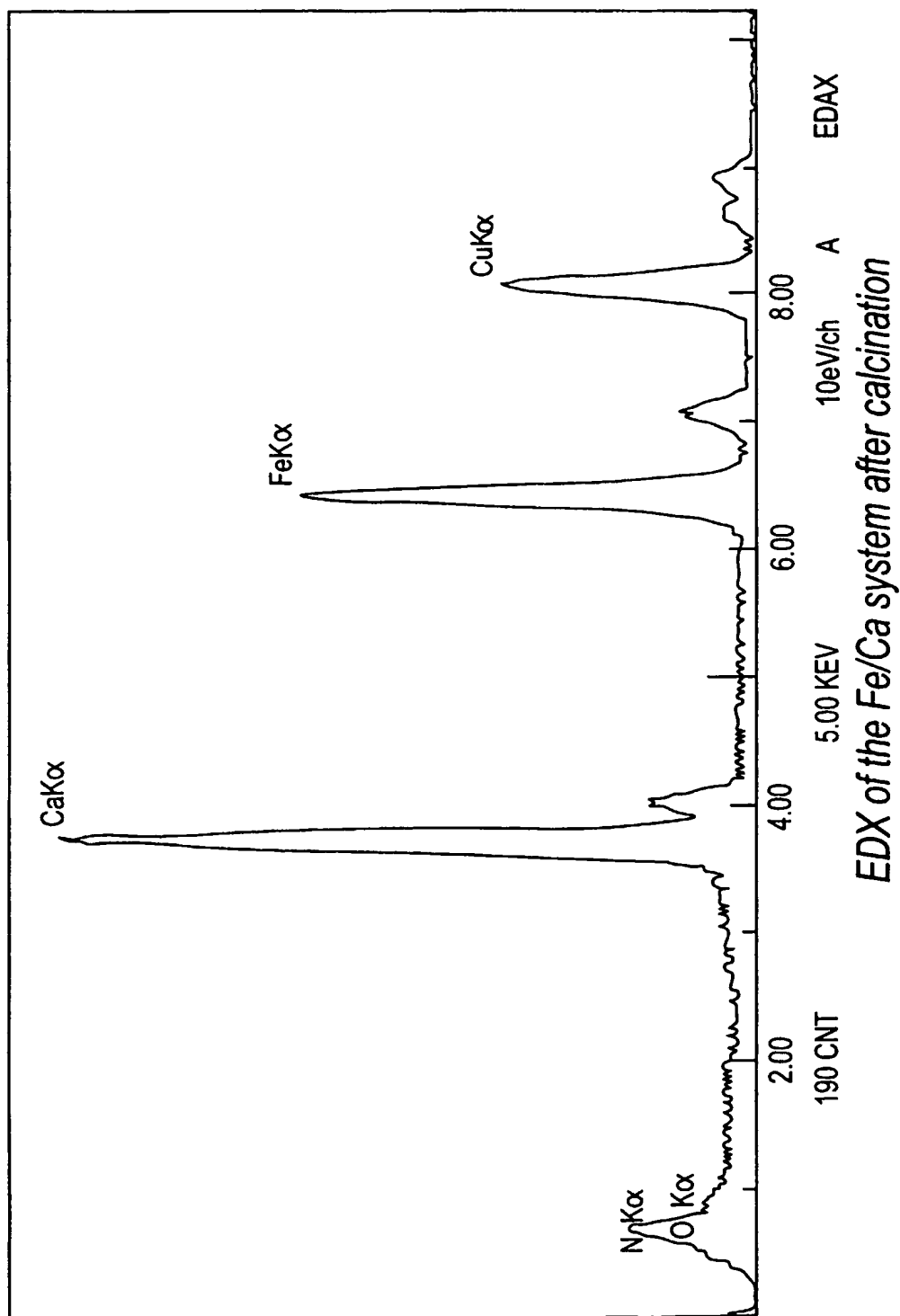
Fig. 14

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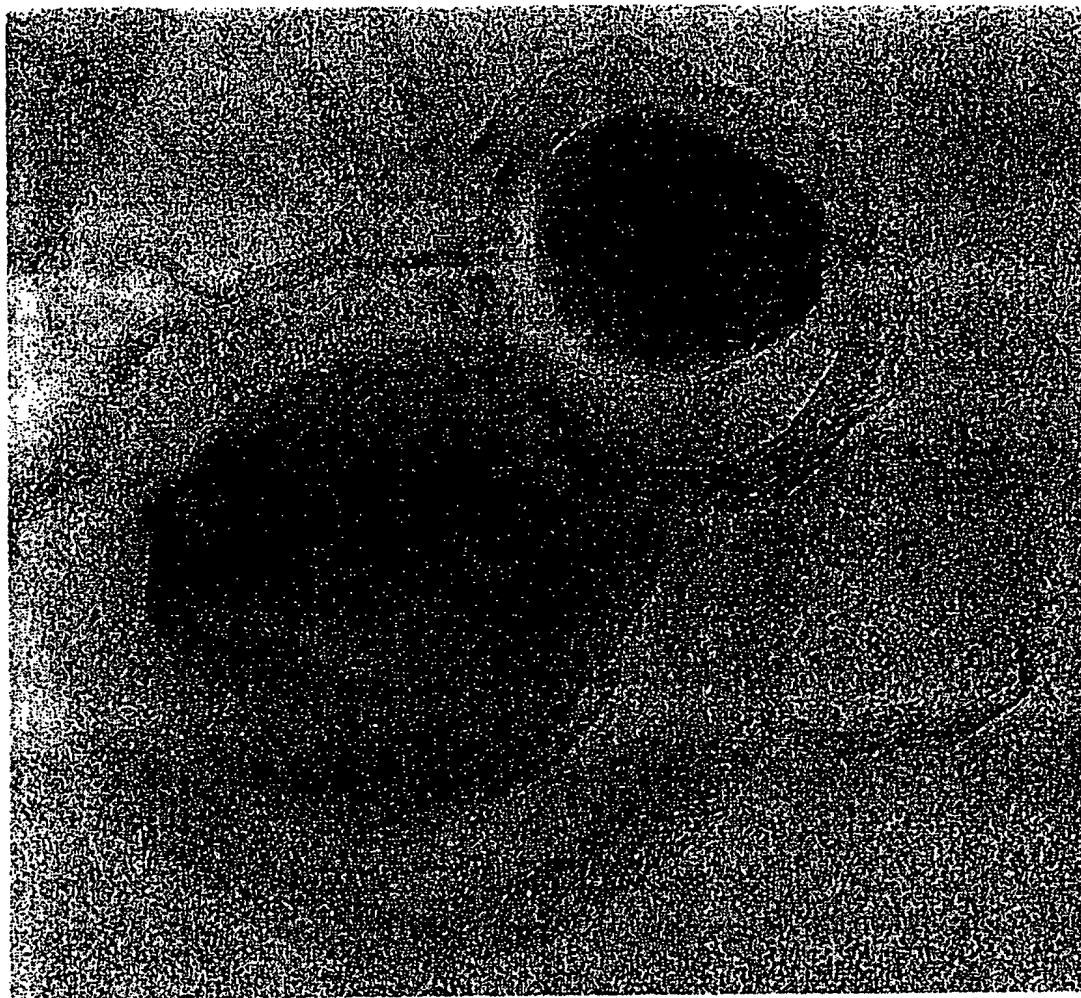


VSM of the Fe/Ca system after calcination. **Fig. 15**

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**Fig. 16**

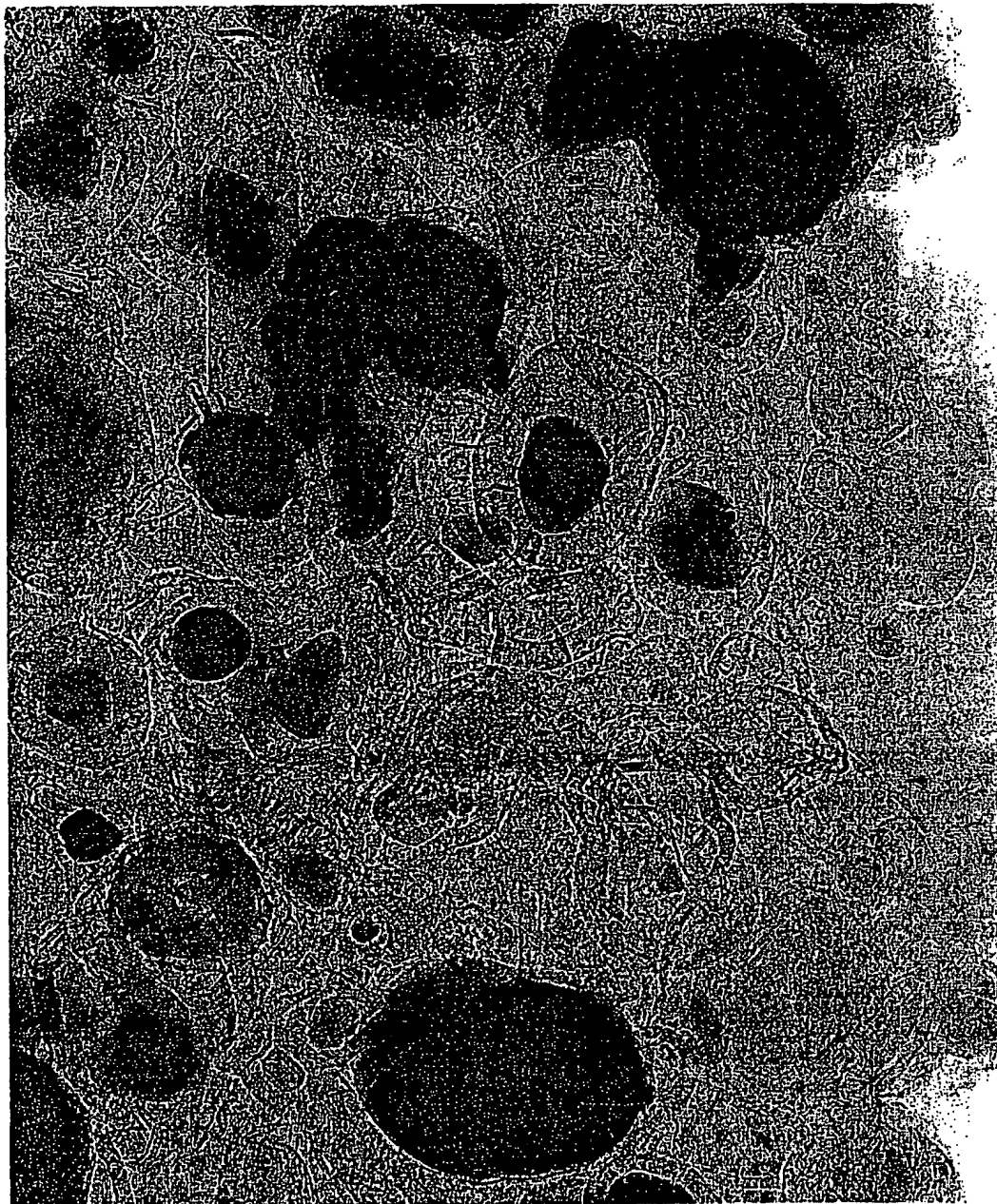
19/22



High resolution TEM micrograph of the Fe/Mn system after calcinations (x 1,000,000)

Fig. 17

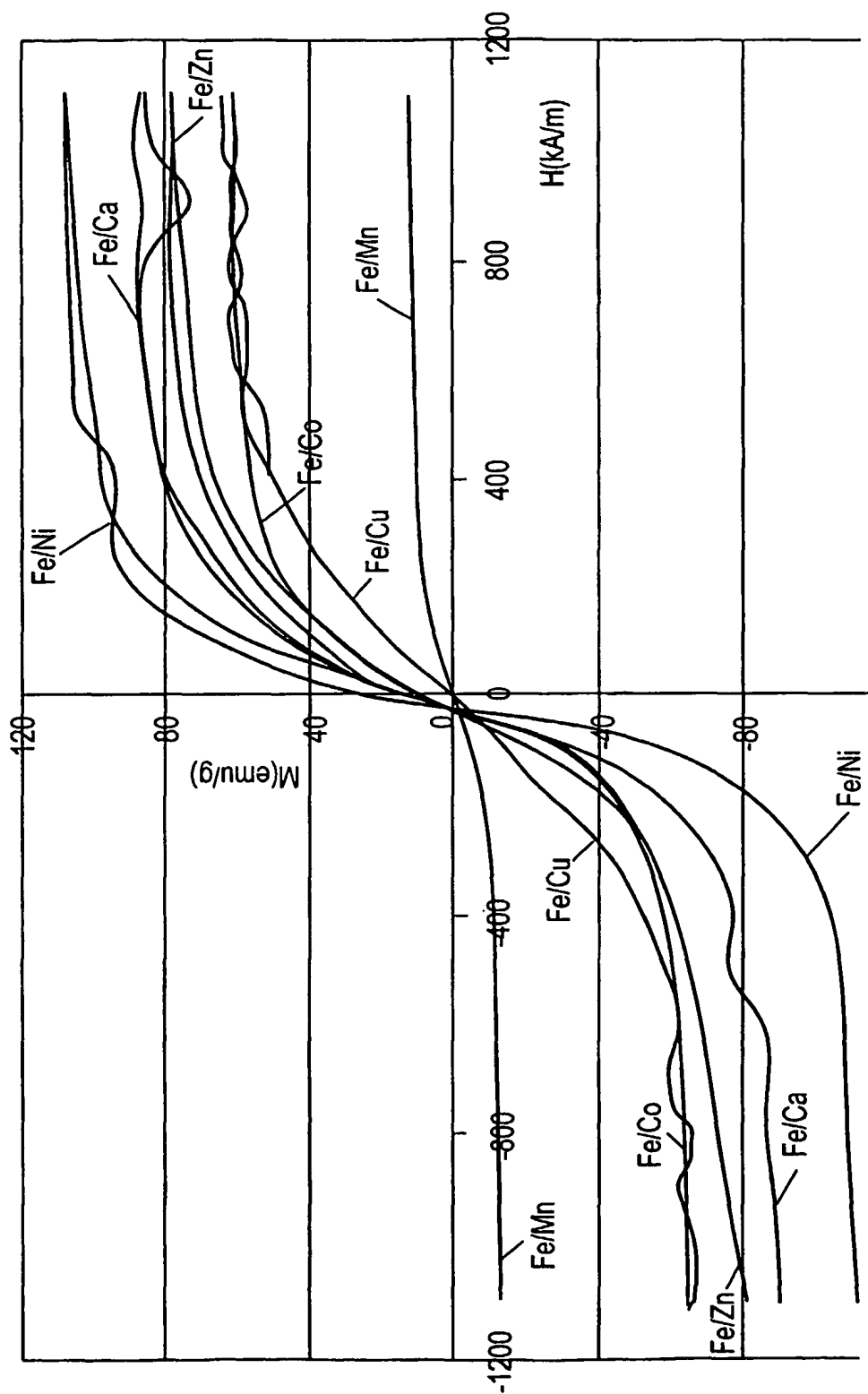
20/22



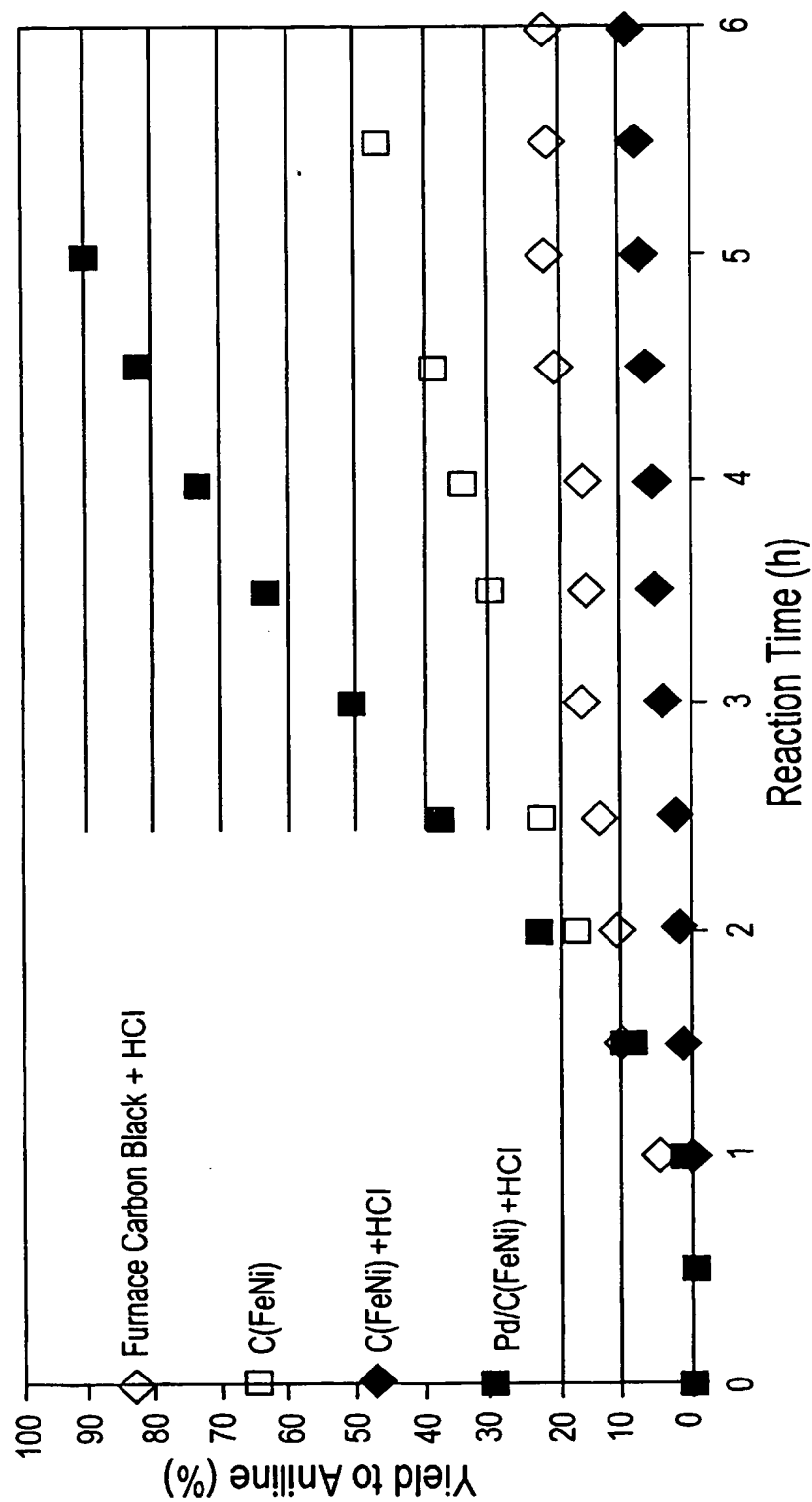
TEM micrograph of the Fe/Mn system after calcinations (x 200,000)

Fig. 18

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*Fig. 19*

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*Fig. 20*

INTERNATIONAL SEARCH REPORT

Internat. Classification No.

PCT/GB 03/00023

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/30 B01J21/10 B01J37/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 46782 A (GEUS JOHN WILHELM ;U CAT B V (NL); UNIV UTRECHT (NL)) 16 September 1999 (1999-09-16) cited in the application example 1	1,17
A	--- PATENT ABSTRACTS OF JAPAN vol. 1997, no. 07, 31 July 1997 (1997-07-31) & JP 09 086915 A (AGENCY OF IND SCIENCE & TECHNOL), 31 March 1997 (1997-03-31) abstract	1,17
A	--- US 5 547 748 A (DYER MARK J ET AL) 20 August 1996 (1996-08-20) example 1 -----	1

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Date of the actual completion of the international search

26 May 2003

Date of mailing of the international search report

05/06/2003

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Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/00023

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			AU 2861099 A	27-09-1999
			EP 1062672 A2	27-12-2000
			JP 2002507055 T	05-03-2002
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			ZA 9901800 A	04-10-1999
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JP 09086915	A	31-03-1997	JP 2782589 B2	06-08-1998
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US 5547748	A	20-08-1996	NONE	
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